U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-266 703

3rd USA/USSR Symposium on Intensification of Bio-Chemical Treatment of Wastewaters Held at Vodgeo Headquarters, Moscow, USSR on 23-24 Aug 1976

Environmental Protection Agency, Washington, D.C.

Prepared for

United States-Union of Soviet Socialist Republics Working Group on the Prevention of Water Pollution from Municipal and Industrial Sources

Aug 76

BIBLIOGRAPHIC DATA SHEET

1. Report No.

2.

3. Recipient's Accession No.

4. Title and Subtitle
USA/USSR Symposium on Intensification of Bio-Chemical
Treatment of Wastewaters
three in a series

5. Report Date
August 1976

6.

7. Author(s)

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
U. S. Environmental Protection AGency
Office of Water Program Operations
Municipal Construction Division WH-547
401 M St., SW Washington, DC 20460

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Address
Working Group on the Prevention of Water Pollution from
Municipal and Industrial Sources
~~Washington, D~~.C.

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstracts

The third cooperative USA/USSR symposium on the Intensification of Bio-chemical Treatment of Wastewaters from Municipal and Industrial Sources was held in Moscow USSR at the Vodgeo headquarters on August 24 through 25, 1976.

The fifteen papers that were presented at the symposium (seven US and eight USSR) are reprinted in English in this volume.

17. Key Words and Document Analysis. 17a. Descriptors

Bio-chemical Oxidation Kinetics
Biochemical Oxidation Technology
Control of Nitrogen
Activated Sludge process
Artificial Aeration

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group

18. Availability Statement

19. Security Class (This Report)
UNCLASSIFIED

20. Security Class (This Page)
UNCLASSIFIED

21. No. of Pages
92

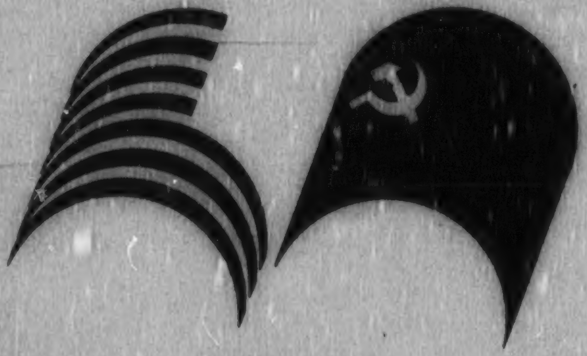
22. Price PC A05
MF A01

FORM NTIS-35 (REV. 10-73) ENDORSED BY ANSI AND UNESCO. THIS FORM MAY BE REPRODUCED USCOMM-DC 8265-P74

PB 266 703

USA-USSR
WORKING GROUP
ON THE PREVENTION OF
WATER POLLUTION
FROM MUNICIPAL AND
INDUSTRIAL SOURCES

Vodgeo Moscow, USSR
August 23-24, 1976



USA·USSR

SYMPOSIUM ON

INTENSIFICATION OF BIO-CHEMICAL TREATMENT OF WASTEWATERS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY WASHINGTON D.C. 20460

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

USA-USSR WORKING GROUP on the Prevention of Water Pollution from Municipal and Industrial Sources

Symposium on Intensification of Bio-Chemical Treatment of Wastewaters

Vodgeo
Moscow, USSR
August 23-24, 1976

1 (a)

INDEX

Preface 1

Opening Address - Mr. John T. Rhett 2

Papers Presented at the USA/USSR SYMPOSIUM

Yakovlev, S.V., Skirdov, I.V., Rogovskaya, C.I., and Shvetsov, V.N. (Vodgeo), *Kinetics of Biochemical Oxidation* 4

Cywin, Allen (US EPA), *Chemical Additions to Biological Treatment of Petroleum Refinery Wastewater* 16

Shifrin, S.M., Mishookov, B.G., Ivanov, G.V. and Golookovskaya, E.K. (Leningrad), *The Trends in Intensification in Biochemical Treatment of High Density Wastewater* 22

Lacy, William (US EPA), *Steel Industry Wastewater Treatment Using Biological-Chemical Technology* 25

Gerber, V.Ya (Bashkirian Scientific Research Institute of Petroleum Refining, USSR), *Facilities Improvement for Biochemical Treatment of Petroleum Refinery Wastewater* 30

Rosenkranz, William (US EPA), *Biological Methods for Control of Nitrogen in Municipal Wastewaters* 32

Skirdov, I.V., Shvetzov, V.N., Bondarev, A.A., Lurje, B.I., Bereykina, N.G., Katchkova, S.E. (USSR), *Operation Experience of Oxytanks* 36

Sebastian, Frank and Lachtman, Dennis (Envirotech), *Improvements for Kraft Pulp and Municipal Treatment Processess* 41

Yakovlev, S.V. and Karjukhina, T.A. (USSR), *Biological Wastewater Treatment in the Presence of Steroid Compound* 50

Harper, Fred (Orange County Sanitation Districts, California) *A Comparison of Conventional Activated Sludge Process and Pure Oxygen Activated Sludge Process for a 75 MGD Secondary Treatment Facility* 54

Skirchiavichus, A.L. (The Kaunas Polytechnic Institute of Snechkus A.) *Studies of Artificial Aeration in the Lithuanian SSR* 60

Adams, Carl (Associated Water and Air Resources Engineers, Inc) and Sumner, Billy (American Consulting Engineers Council, Barge, Waggoner, Sumner and Cannon), *Wastewater Treatment Concerns of the Organic Chemicals Industry in the United States* 62

Skirdov, I.V., Shvetzov, V.N., Morosova, K.M., Gubina, L.A. (USSR), *Biochemical Treatment of Highly Concentrated Wastewaters From Wool-Scouring Operations* 70

Love, William (Hampton Roads Sanitation District, Norfolk, Virginia), *Analytical and Process Improvements in Biological Treatment of Municipal Wastewaters* 74

Ysrshov, A., Kyghel, M., Zemlyak, M. (Candidates of Sciences), *Development and Improvement of the Municipal Sewage Biological Treatment Facilities* 78

Protocol 80

Appendix I Participants 81

Appendix II Reports 82

Appendix III Program 82

Appendix IV Itinerary 84

PREFACE

The third cooperative USA/USSR symposium on the Intensification of Bio-Chemical Treatment of Wastewaters from Municipal and Industrial Sources was held in Moscow, USSR at the Vodgeo headquarters on August 24 through 25, 1976. This symposium was conducted in accord with the protocol of the Fourth Session of the Joint USA/USSR Commission held in Washington, D.C. from October 28 through 31, 1975.

This symposium was sponsored under the auspices of the Working Group on the Prevention of Water Pollution from Municipal and Industrial Sources. The United States delegation was headed by John T. Rhett of the United States Environmental Protection Agency and the Soviet delegation by Professor S.V. Yakovlev of the Department of Vodgeo in the Soviet Union.

The fifteen papers that were presented at the symposium (seven US and eight USSR) are reprinted in English in this volume.

This volume is reprinted in English in accord with the protocol signed by the delegation leaders on September 4, 1976 in Moscow, USSR.

OPENING ADDRESS

John T. Rhett

Introduction

This third symposium of the U.S./U.S.S.R. "Working Group on the Prevention of Water Pollution from Municipal and Industrial Sources" represents another milestone in the advancement of cooperation between our nations in improvement of the earth's environment. It is said that cooperation in environmental matters can serve as a model of how two countries can cooperate for the mutual benefit of themselves and of all nations. Certainly this has proven to be so in our group where so much progress has been made so swiftly in the areas to which we have addressed ourselves.

It is especially significant to the world that our activities have been directed not only to municipal treatment of sanitary wastewaters, but also to industrial wastewaters. As our countries are the two nations with the largest gross national products of the world we have the greatest need to treat industrial wastes as well as the greatest opportunity to learn how methods of treatment can be improved so that there is no threat to the environment. Not only industrial strength is characteristic of our nations, but also the need to give world leadership in industrial environmental control.

U.S. Municipal Wastewater Treatment Systems

On the part of the United States, we have embarked on one of the largest public works programs in the history of the world in order to bring our waters up to fishable and swimmable standards by 1983. This endeavor involves 18,000 municipalities with a combined population of over 200 million people. Our Congress has provided $18 billion in grants to municipalities in order to initiate the clean-up program. With this $18 billion, which represents 75% of the total construction cost of $24 billion, 9,000 municipalities will have established their sewerage systems by next year. However, less than 40 percent of the 1977 population will be served by secondary treatment or some higher level necessary to meet water quality, principally because the large cities will not have had time to complete construction. We still have a long way to go, and it will require additional large sums of money to accomplish our goal. Already, however, we have 7,126 active projects underway, with 10,500 slated for next year.

One of our principal tasks has been to keep the municipalities enthusiastic and moving on the program of cleaning up their waters. We have found it necessary to have seminars, briefings, and conferences that bring the message to every potential community that is eligible for Federal assistance. This endeavor has worked remarkably well and has enabled national goals and standards to be integrated into local government aims and needs. We are pleased by the progress that has been made in this area and the cooperation that has been fostered.

U.S. Industrial Wastewater Treatment Systems

Environmental concerns have also been integrated into the decision-making process in industry. Many industries have actually found it more profitable to operate with environmental concerns in mind and to recycle and conserve water used in their processes and to recover valuable resources from wastewaters. Together government and industry expended about $15.7 billion in pollution control last year and a goodly portion of this amount was in control of wastewaters. Of special note is the fact that a new pollution control industry has been created which employs some one million workers.

Of course, our municipalities are also involved with treating industrial wastes, just as Soviet industry and municipalities cooperate in combined treatment systems. Our working group has made significant contribution to making knowledge known about how pretreatment of industrial wastes can be accomplished so that municipal systems can operate efficiently in treating the remaining industrial wastewaters.

First Working Group Symposium

I would now like to comment on the progress that has been made by the Working Group on the Prevention of Water Pollution from municipal and industrial sources.

Our first cooperative U.S./U.S.S.R. symposium on municipal and industrial wastewater sludge, held in Moscow in 1975, was a fundamental contribution to ways of handling the increasing amounts of sludge that are being generated by our improved wastewater treatment methods.

Depending upon the composition of a wastewater treatment plant's sludge, the quantity involved, and the disposal method, disposal of sludge can have an important impact on the environment. It is therefore essential for wastewater treatment installations to consider the proper disposal of the sludge that is produced. In fact, this is one of the most important factors that must be considered in the design of any wastewater treatment facility.

Our insight in making sludge the first topic of our series of symposia was a fortunate one. Time has proven that the method of disposal of sludge is both a problem and an opportunity. As our symposium indicated, the ultimate use of sludge as a valuable resource for many worthwhile uses has to be the ultimate goal of our efforts. I believe that we have made significant progress in the last year. In fact, EPA has established a sludge Task Force which is just about to issue its report on developments in this area and the first symposium provided excellent background material for its efforts.

Second Working Group Symposium

Our joint symposium last year at Cincinnati, Ohio examined physical/chemical treatment of wastewaters from municipal and industrial sources. It is here that we are at the cutting edge of research and innovative methods in wastewater treatment. The methods discussed at the symposium are essential tools with which to work to provide the most cost-effective treatment of difficult wastes while at the same time providing the means to make possible the recycling and re-use of water resources. More and more, our water resources are becoming scarce relative to uses that have to be made of them. There is, of course, a definite limit to the amounts of water that are available from nature. Our only means of meeting the need for increased use is through conservation and re-use. The physical/chemical treatment methods offer us unparalleled opportunities for re-use, as set forth at our symposiums. We can be sure that that symposium will always be a landmark in progress in treating wastewaters, if only for its contributions to the science of re-use. But, of course, the symposium was significant in a multitude of other areas of scientific advance in wastewater treatment. The symposium papers will need to continue to be mined for valuable insights, data, and practical applications.

Third Working Group Symposium

Our third symposium, which we have convened today, on "Intensification of Bio-Chemical Treatment of Wastewaters", is another building block to the success of the mutual efforts of our nations in bio-chemical methods of treatment. Treatment methods are beginning to show important advances and are a key to many difficult cases of treatment needed.

It is especially notable here that a paper will be presented from each of four related industry groups: chemical technology; pulp and paper; femorous metallurgy and petroleum refining; and petro-chemical. In addition, municipal treatment processes will be discussed that use bio-chemical treatment. These industrial groups represent a great percent of the total wastewater flows to be treated by industry. As such, we are really covering the problems and opportunities of almost all of the industrial flows that must be considered. Therefore, we can make real advances in exchanging knowledge of bio-chemical methods and processes for treating industrial and municipal wastewaters. I wish you great success in your efforts.

Fourth Working Group Symposium

I look forward to our fourth working group symposium which will be convened in January 1977, again at the EPA Cincinnati research complex. The subject of the symposium will be Physical-Mechanical Wastewater Treatment." This subject area will continue to round out our efforts to have a comprehensive view of the subject field of municipal and industrial wastewater treatment methods and opportunities. Fortunately, you will be able to see our new research facility at Cincinnati in full operation. You will remember that in November of last year it was still being completed and was unoccupied. We are happy that we are able to extend to the working group an invitation to attend the second Cincinnati meeting.

Conclusion

My review of the accomplishments of the symposia and visit to the municipal and industrial treatment works of both our countries, leads me to conclude my remarks by expressing a certain amount of amazement that we have been able to progress so far in a relatively brief time. We have approached our mission in a spirit of cooperation and creativeness. We have tackled first things first and have made headway by our industrious and inspired efforts. We have more than fulfilled the assignment that was placed upon us, yet there is further progress that we can mutually undertake. I congratulate you on all of your efforts and results. Let us now move forward even more in improving our own and the world's environment.

Kinetics of Biochemical Oxidation

by Yakovlev S.V., Skirdov I.V., Rogovskaya C.I. and Shvetsov V.N.
All-Union Scientific Research Institutes VODGEO

In the near future biological methods will continue to play the principal role in the main body of wastewater treatment technology due to a number of advantages the biological treatment has as compared to the physical-chemical methods known.

It should be noted however that the biochemical treatment method has not yet exhausted its abilities.

At present the improvement of the process by means of it being affected by external factors is considered to be the most practicable.

Methods of the biological treatment process improvement in aeration tanks by increasing either concentration of activated sludge microorganisms or dissolved oxygen concentration (or its partial pressure) as well as increasing the substrate concentration in first stages of the process carried on in plug-flow aeration tanks have become a practice in sanitary engineering.

The potential abilities of this method may be revealed in full measure during the studies of the process kinetics taking into account interrelation of the main factors.

In the cells of microorganisms of activated sludge, which is the main agent of the biochemical treatment process, many enzyme-catalysed reactions occur simultaneously, the enzymes being closely linked together thus forming complex polyenzymic systems. The peculiarity of biological enzymatic systems is their ability to self-regulation.

Having the data about the principles of such self-regulation it is possible to simplify the complex chains of biochemical reactions essentially.

Under stationary conditions the amount of the material passing through each separate stage of the process must be the same, so the rates of each separate reaction must be equal too. Under these conditions the rate of the process will depend on the rate of the slowest reaction. This concept developed by Ierusalimsky (1) was called "the minimum principle." It is postulated in it that "the rate of the total process depends upon the rate change in the slowest stage only" while the rate increase in the other stages doesn't affect the process. The minimum principle explains such peculiarities of enzymatic systems as their low conversion and saturation. In stationary conditions the minimum principle allows to follow only key reactions without taking into account many secondary ones.

As distinct from non-enzymic reactions the enzyme-catalyzed reaction rate increases with a gradual slowing-down rather than proportionally to the substrate concentration increase and reaches a certain maximum, the value of which depends on the enzyme concentration.

Kinetics of the enzymatic reactions is based on the assumption that there is some enzyme-substrate complex and that the reaction rate depends on the rate of its degradation. The complex is assumed to be formed instantly, because its concentration is constant and defined by thermodynamic equilibrium between the enzyme, substrate and this complex.

Assuming that the completion of an enzymatic reaction is preceeded by formation of enzyme-substrate complex Nichaelis and Menten (2) presented it by the following scheme

$$S + E \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} S\,E \underset{K_{-2}}{\overset{K_2}{\rightleftarrows}} P + E$$

and thus obtained the well-known Equation

$$V = \frac{V_{max} + S}{K_s + S} \qquad (1)$$

where V is the reaction rate at substrate concentration S;

V_{max} maximum reaction rate without substrate limiting;

K_s reaction constant.

In works by Monod (3) and Ierusalimsky (1) the biomass growth rate (μ) was shown to be described by the analogous equation:

$$\mu = \mu\ max \ \frac{S}{K_s + S}, \qquad (2)$$

where $\mu = \frac{d_x}{dtx}$; x is the microorganisms concentration.

The relationship between substrate uptake rate and biomass growth rate is usually expressed by the dependence:

$$\frac{dx}{dt} = -y \frac{ds}{dt},$$

where y is the proportionality factor, characterizing biomass yield per unit of the substrate consumed (economic coefficient).

Keeping in view dependence 2, the equation for the substrate uptake rate can be written in the form:

$$-\frac{ds}{dt} = \frac{1}{y} \frac{max S}{K_s + S} x. \qquad (4)$$

This equation and its modifications were successfully used by Hinshelwood, Herbert, Dawning, Benedek, Gunter et al (4, 5, 6, 7, 8) in mathematical models of biological wastewater treatment systems.

A number of investigators stick to different, fully empiric dependences, based on so-called two-phase theory of substrate removal, proposed by Garret and Sawer (9). This theory was used later by Eckenfelder, McCabe, Korolkov and Bazyakina (10, 11, 12).

In accordance with this theory and on the basis of experimental data the process of activated sludge microorganisms growth can be conditionally divided into two phases: in the first one the substrate concentration exceeds the limit, necessary for the complete saturation of enzymic systems, in the second one the saturation rate decreases as the substrate is removed.

For the first phase the following type of Equation is assumed:

$$\frac{dx}{dt} = K_1 X \qquad (5)$$

and for the second one

$$\frac{dx}{dt} = a \bullet K'_2 x \bullet S, \qquad (6)$$

where a is an empiric coefficient and coefficients K'_2 and X are combined:

$K'_2 x = K_2$.

In a transition point of these two phases where the growth rates are equal according to Equations 5 and 6 $K_1 x = aK_2 S$.

The further development of this theory by Wuhrman et al (13) as applied to the multicomponent substrates has led to the hypothesis according to which the waste water substrate removal curve is the superposition of direct line segments characterizing uptake of a particular substrate compounds by activated sludge.

With the help of this hypothesis a satisfactory agreement of the calculated data with the experimental ones can be obtained as shown by the work of Evilevitch et al (14).

It should be noted however that the use of theoretical regularities known in modern biochemistry and microbiology gives more possibilities for the mechanism of the biological treatment process to be revealed as compared to empiric formulae which have a particular character. It must be born in mind that either for a single cell or for a complex biocoenosis of activated sludge oxidizing multicomponent substrate the minimum principle is apparently valid, that is the limiting of the process by one, the most slow reaction.

Information obtained from the literature can't give a clear unambiguous answer to the question about the character of the relationship between the MLVSS and the rate of organic matter oxidation in aeration tanks.

A number of recent investigations (15, 16) show that there is no proportional relationship between the MLVSS and the rate of oxidation; sludge activity measurably decreases when its concentration increases. Analogous phenomenon is observed during the propagation of living organisms population in the process of biological synthesis as well. In general this phenomenon can be caused by the following reasons:

—the mass exchange deterioration due to the change in reological properties of mixed liquor;

—interspecied competition of microorganisms;

—microorganisms development suppression by products of their metabolism.

The lack of information referring to the effect of the MLVSS concentration upon the rate of biochemical oxidation does not permit drawing a conclusion about the mechanism of this phenomenon.

It should be noted that there is no agreement in the works devoted to the dissolved oxygen concentration effect upon the activated sludge microorganisms metabolism, and the experimental results are very contradictory. Some investigators point out to the existence of the dissolved oxygen critical concentration above which the oxygen effect on the process is not observed (17, 18, 19). Concrete values of this concentration according to the data obtained by different investigators have an essential error. In other works mainly referring to the enzymes production, a suppressive or toxic effect of high D.O. concentrations was observed (20, 21). In a number of recent works dealing with the problem of oxygen use for biological treatment (22, 23) an evident positive effect of the oxygen concentration up to [illegible]0 mg/l was marked. In this case the rate of substrate removal increases and the settling properties of mixed liquors is being improved.

Disagreements in the evaluation of oxygen effect upon the biological treatment process can be explained by the influence of many secondary factors badly affecting the experimental results, by the insufficient variation range of the parameters under study and by the absence of uniform methods and suitable equipment for such investigations.

It should be outlined especially that the theoretical aspects of D.O. and MLVSS concentrations effect on the kinetics of the biological treatment process have been studied insufficiently.

It is known from biochemistry that the molecular oxygen can be involved in the cellular metabolism in three ways:

1. as a terminal electrone acceptor in the respiration chain;

2. at the direct incorporation into the substrate to be oxidized;

3. for direct acceptance of hydrogen from dehydrogenases with the hydrogen peroxide formation, without respiration chain being involved.

The molecular oxygen role in the cellular metabolism is extremely great, because it is one of the most important components of the processes providing the microorganisms with the energy and material for their biosynthesis.

The molecular oxygen does not only take part in the final substrate oxidation but oxygenates a large number of organic compounds in the initial stages of their metabolism, and thus enables their being used by microorganisms.

Due to the conjugation of oxidation and phosphorilizing oxygen influences on the energetic level practically all enzyme-catalyzed processes proceeding in the cell. On this basis one can assume that the oxygen effect must be described mathematically by equations of enzymatic reactions. Since the substrate and oxygen take part in the oxidation process, this equation must be one of the bisubstrate enzymatic reaction equations the type of which may be determined after the analysis of experimental data.

The attention of investigators in the field of wastewater treatment is especially attracted by the theoretical aspects of the regularity between biochemical oxidation of organic compounds and their physico-chemical structure, kinetics of its biochemical destruction and enzymatic properties of the microorganisms involved in the process.

When studying the effect of the material structure on the biochemical destruction process Winter (29) has drawn a conclusion that in most instances the rate of destruction decreases as the molecular weight increases. The oxidation rate decrease was observed in the homologous series of alcohols with lengthening of hydrocarbon chains. By the author's opinion the chain branching decreases the oxidation rate essentially. It is valid, however, for the aliphatic series only.

An unimportant change in the structural formula of a substance produces a considerable effect on biological oxidation. Substances with the hydroxide radical are oxidized readily.

When studying the effect of various functional groups on the rate of the organic compounds destruction Winter marks the continuous decrease in the rate of the biological degradation involving the following succession: — SO_2H, — OH, —COOH, —NH_2, —CN, —CHOH, —CH_2OH, —OOC, —CH_2, —CH_3.

Among the aromatic compounds benzene is the least biodegradeable; compounds with a short side chain such as toluene and ethylen benzene are a little more biodegradable. Compounds with longer side chain inhibit biological destruction almost completely.

The information available gives only approximate data concerning the effect the molecular structure of substances produces on their biochemical oxidation parameters.

In the majority of the well-known works (30, 31) the quantitative evaluations are absent, many of the data are contradictory since the investigations were conducted in different conditions and under different methods. Criteria for the experimental data evaluation various as well.

These circumstances caused the necessity for special complex investigations to be conducted including technological, miclobiological and oxidation process of organics belonging to different classes.

Methods of Investigations

It was shown previously that the metabolic activity of the microorganisms depends on the external parameters and first of all on the concentration of a carbon substrate and D.O. concentration.

The lack of only one component in the environment causes decrease in the metabolic activity, that is why investigation of the external parameters affect the so-called "limited" media are usually used, where the amount of only one component under investigation is varied and the other components necessary for the cell growth are present in excess.

In modern practice of biological studies in general and studies of kinetics of wastewater organics biochemical oxidation in particular, two approaches are used: the continuous cultivation method and the method of investigations in batch conditions, each of them having its own advantages and shortcomings.

On the basis of the properties of the subject under investigation and the aims of investigations a method must be chosen capable of providing the maximum reliable information with the minimum of efforts and expenditures spent.

Activated sludge has a number of specific properties the most important of which are its biological inertia and adaptation.

Biological adaptation of activated sludge is such a phenomenon when the cell gradually rather than immediately adopts to the environmental change. Increase in the cell growth rate is connected with the preliminary increase in the amount of ribosomes and other organelles responsible for protein synthesis. The process takes the time comparable to the time for cell reproduction.

Adaptation of microorganisms to the particular environmental conditions is connected with the reformation of the cell enzymatic apparatus as well as the change in the specied composition of the activated sludge as a result of natural selection and mutation. When environmental conditions are changed adaptation causes corresponding changes in biochemical properties of the culture.

When evaluating the microorganisms properties one should bear in mind that the substrate biological destruction is carried out by enzymatic reactions the duration of which amounts to seconds.

As compared to the synthesis reactions of enzymatic macromolecules or to the processes of the cell working apparatus formation (ribosomes, mitochondrions, membranes) the duration of which amounts to hours enzymatic reactions may be considered very rapid ones.

Comparing the continuous- and batch-flow methods it should be mentioned that in the closed system of batch studies simultaneous change of several parameters with time (substrate, oxygen, metabolite and biomass concentrations etc.) is inevitable. This makes the evaluation of some parameters under investigation difficult. Besides, the phenomenon of biological inertia can sharply reveal itself here.

The continuous-flow cultivation method does not possess the above mentioned disadvantages of the batch method because it theoretically allows to keep the biological system studied in the given equilibrium state for unlimited period of time. However when the continuous-flow process is carried on in practice serious technical difficulties can occur, breaking its stability and lowering its accuracy and the reliability of experimental data. These difficulties are caused by the necessity for the microamounts of substrate elements to be dosed precisely as well as the necessity for stabilization of biomass concentration, pH, aeration intensity or O_2 concentration etc. Any reliable control devices for many of these parameters have not been available yet.

On the other hand the change of external parameters in a continuous-flow reactor inevitably leads to adaptation and so to the chape in biochemical properties of activated sludge that interferes with the analysis of the external factors affect on biochemical properties of activated sludge that is upon its enzymatic apparatus.

Thus none of the accepted methods can pretend to be the universal one, each of them has its own field of application.

The continuous cultivation method is expedient to be used for the growth of activated sludge biomass adopted to a certain substrate. This method is irreplaceable for the study of slow adaptation processes.

When the effect of the external parameters upon the sludge enzymatic activity is studied the batch tests are rationaly used.

In batch tests the right choice of the interval in which the process rates are measured is of great importance. It must be small enough in order for the substrate and activated sludge not to take the time to alter significantly and the metabolite concentration not to reach a noticeable value. Besides, this interval must be large enough in order for the equilibrium of the system, that is a quasi-stationary state of kinetic parameters, to be reached.

On the basis of general considerations concerning the methods of investigations into the kinetics of biochemical oxidation the bench-scale studies were carried out on continuous-flow models of aeration tanks of various modifications as well as by means of running "sharp" tests in batch-flow aeration tanks and respirometers.

In continuous-flow conditions the experiments were run for comparison of D.O. concentration and MLVSS concentration effect upon the biochemical oxidation rate for various substrates. The necessity for these experiments to be run was dictated by the desire to bring the results of bench-scale studies close to full-scale conditions since they allow to take account of the activated sludge adaptation to certain substrates and to other external conditions which can take an important effect on the sludge activity and on its physical characteristics, in particular upon the settling properties.

During investigations a regular technological control for the operation of the units was carried on. The microbial content of activated sludges, its physical parameters (such as sludge volume index (SVI), the size and the form of zoogloen), ash content, COD and BOD of the effluent and mixed liquor, MLSS, N, and P content of the effluent were determined. Chemical analyses were conducted by Standard Methods.

A Complete-mixing Aeration Tank

A conventional laboratory aeration tank served as a model of the complete-mixing aeration tank (Fig. 1). Aeration tanks for operation with high MLSS concentrations were rigidly fixed with the settling tanks.

Sludge recirculation was carried on either by a dosing diaphragm pump or at the expense of the difference between volume weights of air-water mixture.

The control for air supply was carried on manually in accordance with the given oxygen profile. The D.O. concentration was determined periodically by an electrochemical sensor.

A Counter-flow Aeration Tank

For determination of the counter-flow efficiency in the process of oxygen absorption and its uptake by biochemical oxidation the model of a counter-flow aeration tank was used.

The counter-flow aeration tank operated in the regime of a complete-mixing reactor; it was a closed circuit comprising two vertical columns made of plexiglass (Fig. 2).

Recirculation of the liquid in the circuit was created by an impeller pump (I) fixed in the upper part of the recirculation column (2). This permits the necessary rates of the downflow in the aeration zone to be obtained (column 3). The rate of recirculation was measured by the head loss in the measuring diaphtagm (5) and was regulated by a valve (6). Influent was fed to the aeration tank through the tubing (7) in the upper part of the aeration column. Either oxygen or air was fed through the porous diffuser (4) in the lower part of aeration zone.

The oxygen profile stabilization was fulfilled by automatization of the air supply system on the basis of D.O. analyser. This system provided the accuracy of D.O. concentration ±1.0 mg O_2/l in the range of this parameter change from 3 to 20 mg/l.

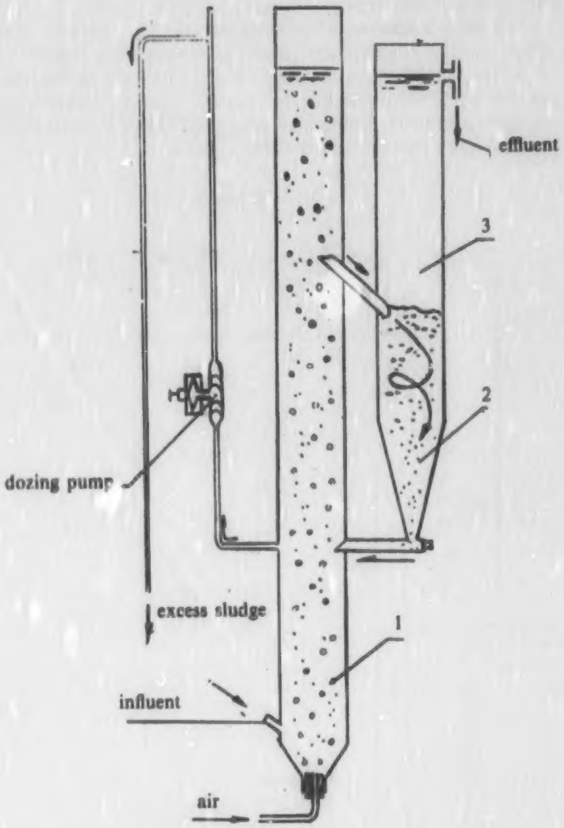


Figure 1 The scheme of a laboratory complete mixing aeration tank.

Respirometers

The large part of experimental data was obtained as a result of investigations conducted on respirometers.

The experiments were run in order to obtain kinetic constants for equation of enzymatic reaction during investigation of the effect, the substrate, oxygen and activated sludge microorganisms concentrations have upon the process.

The respirometric method is widely used in biological studies of such processes accompanied by gas-exchange as plant photosynthesis, metabolism in tissues and respiration of microorganisms.

The advantage of respirometric methods are their relative simplicity and ability of making direct volumetric determinations of the oxygen consumed as well as the continuous observations with the automatic recording of the data.

Negligible inertia allows to work with the small amounts of substrate.

The possibility of simultaneous gas-exchange analysis on the basis of oxygen uptake and carbon dioxide release places the respirometric method in a special position even as compared to such modern methods of investigations as polarography and CO_2 analysis with the help of experimental acoustic analysers.

Warburg manometric instruments were practiced on a large scale for respirometric studies, but they have a number of serious disadvantages such as a small volume of cultural vessels, the impossibility to control during study the following process parameters (oxygen profile, pH, substrate composition and concentration).

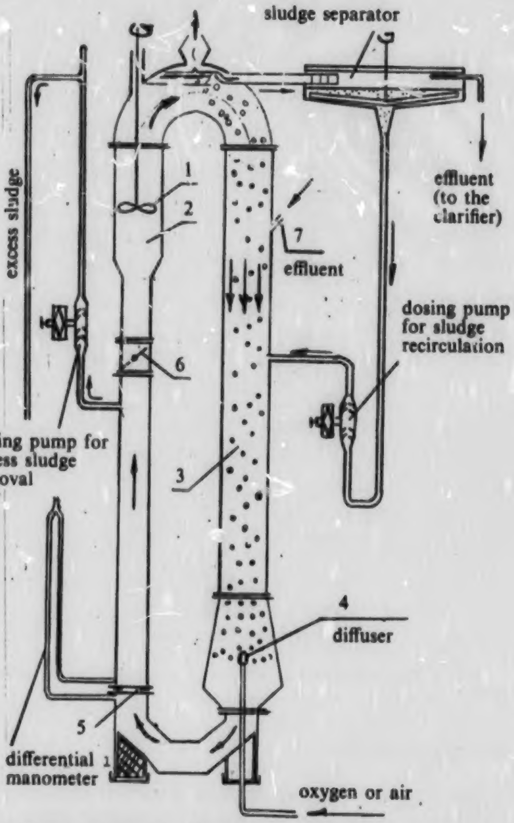

sludge separator
1
2
7
effluent (to the clarifier)
excess sludge
effluent
dosing pump for sludge recirculation
6
dozing pump for excess sludge removal
3
4
diffuser
5
differential manometer
oxygen or air

Figure 2 The scheme of a laboratory counter-flow

Automatic manometric instruments - respirometers - have been used recently. They differ from Warburg respirometers by large volume of cultural vessels, intensive agitation, aeration of the culture and forced absorption of the carbon dioxide released.

In the laboratory of biological treatment a continuous-flow respirometer was developed, the scheme of which is given in Figure 3.

The respirometer consists of the following principal units:

I. The unit of microorganisms cultivation consisting of three hermetic vessels with impeller aerators;

II. The unit of automatic oxygen supply with wet gasholders;

III. The unit of automatic recording of the oxygen consumed;

IV. The unit for carbon dioxide removal from gas mixture with microcompressors and scrubbers;

V. The unit of temperature stabilization with contact thermometers;

VI. The unit of D.O. concentration measurement with the help of D.O. andlysers " -152.003".

VII. Sludge separation unit with vertical settling tanks;

VIII. System of sludge feeding and recirculation with plunger pumps;

IX. pH stabilization system;

X. MLVSS stabilization system.

The respirometer was provided with three fermenters each of them equipped by autonomous systems of air supply, gas purification, temperature stabilization etc. This allows to conduct parallel investigations in a wide range of parameters change as well as technological researches of multi-stage systems of wastewater treatment.

The instrument has the following technical characteristics:

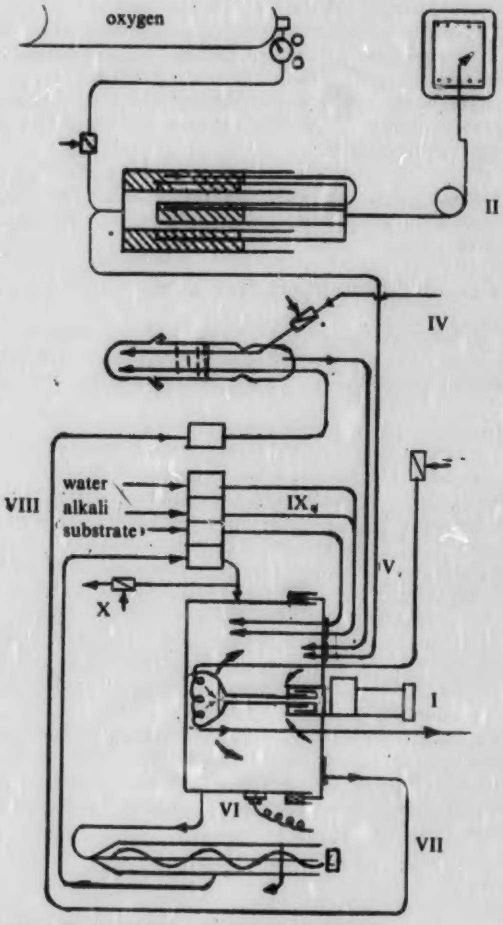

oxygen
III
II
IV
VIII
water
alkali
substrate
IX
V
X
I
VI
VII

Figure 3 Technological scheme of respirometer

1. The fermenter capacity is 3 l.
2. The oxygen feeding accuracy 0.4-0.8 cm^3
3. One scale division of the consumed oxygen recorder - 6 mg/l.

4. Accuracy of the consumed oxygen registration is 1.5 mg/l.
5. The system of D.O. concentration recording is automatic. The accuracy of recording is ±0.5 mg/l when the instrument of the type -152 003 is used. Variation range of D.O. concentration is 0.5-20 mg/l.
6. The system of control for the carbon dioxide released (potentiometric titration with $Ba(OH)_2$ is manual or automatic. The accuracy of CO_2 control is 2 mg/l.
7. Agitation and aeration is carried on with the help of an impeller having 6-step reducer with 200-1500 rev/min.
8. The system of temperature stabilization with heating and cooling is automatic. The accuracy of stabilization is ±0.25°C. The temperature variation range is +5 - +40°C.
9. Feeding of the substrate is carried on by plunger pumps with a continuous change from 0.01 to 10 cm^3/min. The accuracy of feeding is ±5%.
10. Sludge recirculation is carried on by plunger pumps with continuous change in discharge from 0.01 to 10 cm^3/min. The accuracy of feeding is 5%.

Finishing the description of the methods of experiments for biochemical oxidation kinetics determination one should mention a very important peculiarity of biological systems and of activated sludge in particular. This peculiarity is the poor reproducibility of the experimental data. It is caused by two factors: by inaccuracy of instruments and to a large extent by their poor reproducibility (or by so-called time drift) which depends on biochemical properties of activated sludge.

The dispersion of the results caused by the time drift usually exceeds by the order the dispersion caused by inaccuracy of measurements. Relatively law efficiency of strictly successive methods of the experiment planning at the researches of biochemical systems may be explained by this fact.

In order to control disagreement of the results caused by time drift it is appropriate to carry on the experiment in such a way that all values of the parameter under investigation could be studied in one run. Very often it is not possible to do; then several series of tests should be conducted, but in each series one test from the preceeding one should be repeated. On the basis of the test repeated it will be possible to determine the disagreement caused by time drift.

Discussion of the Experimental Results

A. THE SUBSTRATE CONCENTRATION EFFECT

The dependence of the biochemical oxidation process rate on the substrate concentration was studied in continuous-flow conditions on models of complete-mixing aeration tanks and in batch-flow conditions on respirometers.

Such pure chemicals as acetone, normal propyl alcohol, isopropyl alcohol, propionic aldehyde and propylenglycol etc. and real industrial wastewaters of yeast and antibiotics production were used as substrates (as the sources of organic carbon).

In accordance with the working hypothesis the substrate concentration effect on the specific reaction rate is described by the equation of enzymatic reactions (4) the kinetic constants of which may be determined graphoanalytically by Lineweaver - Berk method according to which the initial Equation 4 is presented as reciprocal values

$$\frac{1}{V} = \frac{1}{V_{max}} + \frac{K_s}{V_{max}}\frac{1}{S} \qquad (5)$$

In coordinates $\frac{1}{V}$; $\frac{1}{S}$ the graphical form of this equation is a straight line intersecting the axis $\frac{1}{V}$ in a point of $\frac{1}{V_{max}}$ and the axis $\frac{1}{S}$ in the point of $\frac{1}{K_s}$.

The experimental data plotted to this graph have shown that straight lines have different angles of inclination for different series of tests but intersect in one point ($\frac{1}{-K_s}$). It points out to the fact that one of the reaction components is not homogenous, which is caused by the time drift of activated sludge.

The existence of the common point of intersection shows that the change of the sludge enzymatic activity affects the function V = f(S) in accordance with the law of noncompetent modification, the equation of which has the form:

$$V = V_{max}\left(\frac{K_I}{I + K_I}\right)\frac{S}{K_s + S} \qquad (6)$$

where K_I - kinetic constant of the modificator;
I - modificator concentration.

In reciprocal values the equation can be presented as

$$\frac{1}{V} = \frac{1}{V_{max}}\left(1 + \frac{I}{K_I}\right) + \frac{K_s}{V_{max}}\frac{1}{S}\left(1 + \frac{I}{K_I}\right) \qquad (7)$$

$1 + \frac{I}{K_I}$

It follows from the graphical form of the Equation 7 that the relative activity of sludges for each series of tests differs by the multiplier ( ) and may be evaluated through the ratio of maximum values

$$L = \frac{1/V_1}{1/V_{max}} = \frac{V_{cp_{max}}}{V_{1_{max}}} \qquad (8)$$

where L - sludge activity coefficient for the given series of tests.
$V_{cp_{max}}$ - mean value of V_{max}
$V_{1_{max}}$ - value of V_{max} for the given series of tests.

Values of specific rates with correction for the sludge activity time drift may be defined as

$$V^1 = V_1 \ d_1, \qquad (9)$$

where V_1 is a reduced value of V_{max} for the given series of tests.

The corrected values of oxygen uptake rates and the initial data for their calculation are given in Fig. 4. It follows from the graph that

V_{max} = 99.4 mg O_2/g of VSS/hour.

K_s = 152 mg/l

The terminal form of the function V=f(S) for acetone, oxidized by the activated sludge, is given in the Fig. 5 where the points, obtained by the calculation in accordance with the equation 4, are connected by a curve.

The corrected values of the experimental data agree with the calculated curve, their maximum deviation does not exceed 5 percent.

It should be noted that without time drift these ratios reached 213%.

Analysis of the graphical forms of the function V=f(S) (Fig. 4) shows that curves have smooth slopes with the asymptotic approaching to V max, consequently the approximating of this curve by the two straight lines is wrong from the theoretical point of view.

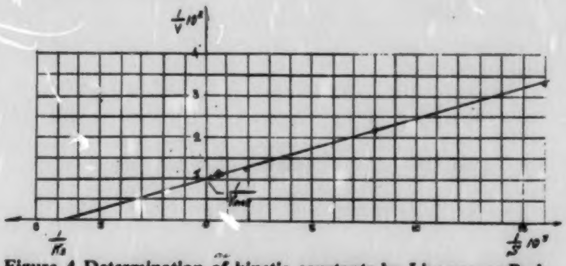


Figure 4 Determination of kinetic constants by Lineweaver-Berk method

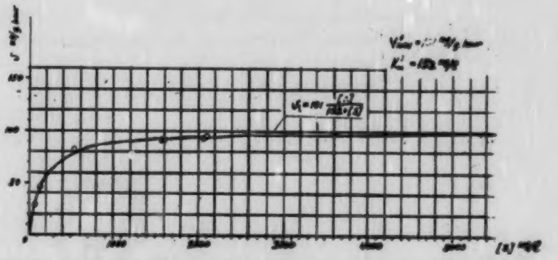


Figure 5 Relationship between oxygen uptake rate and substrate concentration (acetone)

B. THE EFFECT OF THE ACTIVATED SLUDGE MICROORGANISMS CONCENTRATIONS

Experiments for study of biochemical oxidation dependence on the activated sludge concentration were conducted on continuous-flow models of complete-mixing aeration tanks and in batch-flow conditions on respirometers. This dependence was studied for oxidation of such substrates as acetone, butyl alcohol, secondary octyl alcohol, popanol, isopropanel, propioms aldehydr and other pure chemicals and on wastewaters from yeast and antibiotics industries. The investigations were carried out on sludges adopted to these substrates at the sludge concentration varying from 1 to 20 g/l.

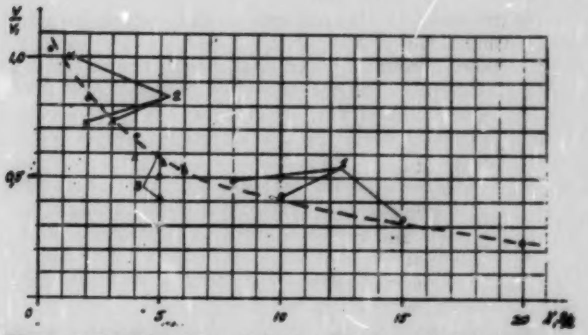


Figure 6 Graphical form of V/V₁ = f(x) for activated sludges acclimatized to acetone (1), secondary actyl alcohol (2), isobutyl alcohol (3).

Experimental data are given in the graph (Fig. 6) as a dimentionless ratio.

$$\frac{n}{1} = f(x),$$

where n is the specific rate of oxidation mg O_2/g VSS/h at MLVSS concentration x;

1 - specific rate of oxidation at MLVSS 1 g/l.

The usage of dimentionless ratio permitted to summarize the data obtained by different methods. The experimental points dissipation is relatively small.

The slope of the curve $\frac{N}{1}$ = f(x) in Fig. 6 shows the significant slowing-down of the biochemical oxidation specific rate as the activated sludge concentration increases.

It was marked before, that this phenomenon may be caused by three factors: mass exchange deterioration due to change in the mixed liquor reological properties, inhibition of microorganisms activity by the products of their metabolism and interspecid competition of microorganisms.

Evaluating the effect of these factors one should mention that the reological properties of mixed liquors (their viscosity) begin to change significantly at their concentrations more than 4-8 g/l(24), but juding by Fig. 6 decrease in the range of its concentrations up to 4 g/l was observed the most clearly.

Besides, in the studies conducted on respirometers mixed liquor was subjected to extremely violent agitation (the impeller's number of revolutions per minute was equal to 1500) which excluded the influence of diffusion processes limited by viscosity. But in these conditions a great decrease in the specific oxidation rate was observed as MLVSS increased. These facts show that it is not possible to explain the decrease in the microorganisms activity when their concentration increases by the change in the reological properties of mixed liquor.

The interspecied competition phenomenon described by the Ferhulst Equation (25) may be attributed to a certain extent to the activated sludge biocoenosis, especially when the substrate is lacked: $\frac{dx}{dt} = x - x^2$, where and are the proportionality factors. However the applicability of this Equation in a wide parameters variation range needs to be proved.

The biomass growth rate in the Ferhulst equation may be expressed through the specific oxidation rate:

$$\frac{dx}{dt} = \frac{1}{y} \quad {}_{n} \quad \cdot x \qquad (11)$$

(the designations are the same).

The specific oxidation rate for a particular kind of sludge at x = 1 g/l and other conditions being invariable is the constant, that is $= E$. (12)
With consideration of Equations 11 and 12 Equation 10 is reduced to the following form:

$$\frac{n}{1} = \frac{Y}{E} (\quad - x)$$

Introducing designations for constant coefficients

$$\frac{Y}{E} \quad = A \text{ and } \quad \frac{Y}{E} = B$$

we obtain

$$\frac{n}{1} \quad = A - B_x \qquad (13)$$

Expression 13 is the direct line equation, that doesn't correspond to the experimental data, given in the plot (Fig. 6).

Hence, the Ferhulst equation can't be applied to the activated sludge biocoenoses.

As previously mentioned the decrease in the sludge activity may be caused by the products of metabolism release, inhibiting biochemical oxidation process which mechanism is described by the following equation

$$V = \frac{V_{max} \cdot S}{K_s + S} \cdot \frac{I}{K_I + I} \qquad (14)$$

where the inhibitor concentration according to Ierusalimsky (26) is proportional to the amount of microorganism biomass.

$$I = \quad \cdot x \qquad (15)$$

The rest designations are the same.

In Equation (14) in conditions of constant substrate concentration or its excess (in these particular conditions a comparison should be made) the members characterizing the substrate effect may be expressed by a constant

$$\frac{V_{max}\ S}{S + K_s} \quad = A \qquad (16)$$

The specific oxidation rate at x = 1 g/l for a particular substrate may be considered a constant as well.

$$V_I = E \qquad (17)$$

Then the Equation will assume the form:

$$V = A \quad \frac{K_I}{Zx + K_I} \qquad (13)$$

The rates ratio with consideration of the assumptions made may be expressed as follows:

$$\frac{V}{V_I} = \frac{A\ K_I}{E(Zx + K_I)} \qquad (19)$$

For the graphical interpretation it is convenient to present the Equation obtained (19) in the form:

$$\frac{1}{V} = \frac{X}{A} \left(\frac{Z}{K_I} \right) + \frac{1}{A} \qquad (20)$$

For a concrete substrate the Z/K_I ratio is a constant.

So we can assume that $Z/K_I =$ where Y is the coefficient characteristic inhibiting of the process by products of metabolism.

Then Equation 20 may be written in the following form

$$\frac{1}{V} = \frac{\quad}{A} \quad x + \frac{1}{A} \qquad (21)$$

As can be seen from Fig. 7 the curves for $\frac{1}{V} = f(x)$ are the straight lines.

This facts serves as the proof of the applicability of bility.

The angle of inclination tangent gives the value of Equation 14.

Analysing the position of direct lines for different substrate concentrations one can note that tg decreases as S increases to a certain value. Hence for determination of coefficient it is necessary to use the data obtained without limiting by substrate.

The specific rate value corresponding to the intersection of direct lines in the plot of $\frac{1}{V} = f(x)$ with the ordinate axis $\left(\frac{1}{V}\right)$ corresponds to the rate A without inhibiting by metabolites.

Thus the analysis of experimental data has shown that the sludge activity decreasing with the increase of its concentration is described by the enzymatic reaction equation with consideration of non-competente inhibiting by metabolites.

It should be noted that inhibiting in a certain range of MLVSS variation is less than the increase in the total sludge biomass activity, so with the MLVSS increase the essential increase in the oxidation capacity of aeration tanks occurs. For certain substrates the dependences of oxidizing capacity on MLVSS is given in the plots (Fig. 8). Optimal value of MLVSS (from the oxidizing capacity point of view) varies in the range from to g/l and depends on the constants of the enzymic reaction equation, characterized by the individual properties of the substrates.

C. EFFECT OF D.O. CONCENTRATION

Technological studies on the models of aeration tanks for investigation of D.O. effect on the biochemical treatment process were carried on with the acetone and phenol used as substrates.

Operation data of counter-flow aeration tanks when the air is fed to one of them and the oxygen to the other one, are given in Table 1.

There is a significant increase in the process rate as the D.O. concentration increases. Thus the acetone specific oxidation rate increased from 3.4 to 112 mg/l/h (2.88 times) as the D.O. concentration increased from 3 to 12.7 mg/l.

Similar data were obtained in tests conducted in batch flow aeration tanks.

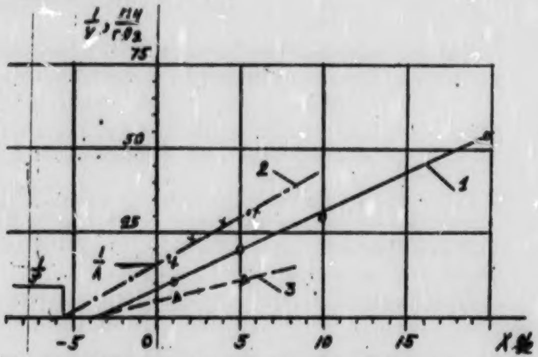


Figure 7 Graphical form of 1/V = f(x) for determination of inhibition factor Y at oxidation of acetone (1) secondary octyl alcohol (2) and isobutyl alcohol (3).

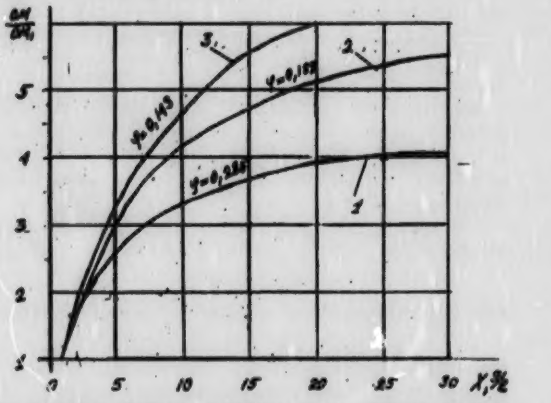


Figure 8 Relative change in oxidizing capacity with the MLVSS increase in aeration tanks at oxidation of acetone (1), octyl alcohol (2) and pyrocatechol (3).

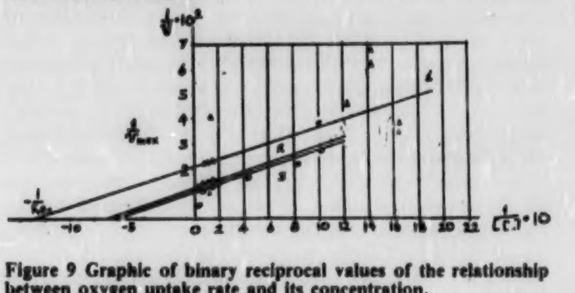


Figure 9 Graphic of binary reciprocal values of the relationship between oxygen uptake rate and its concentration.

1. substrate concentration of 94 mg/l
2. Substrate concentration of 360 mg/l
3. substrate concentration of 450 mg/l

A wide cycle of experiments was carried out on respirometers in batch conditions for a more accurate quantitative evaluation of the D.O. effect. These experiments were carried on with substrate (acetone) concentration varying from 0.5 to 33 mg/l and oxygen concentration varying from 1.0 to 20 mg/l.

The experimental data are given in the plots of functions of V = f(Co). (Fig. 9).

The plots of reciprocal values in coordinates 1/V - 1/S were used for identifying the mechanism of D.O. effect.

It was noted in a number of recent works (27, 28) that the process of oxygen and substrate interaction may be described by several mechanisms. The mechanism of a two stage substitution is possible, where the reduced enzyme group reacts with the products of respiration chain.

The following equation corresponds to this mechanism:

$$\mathcal{Y} = \mathcal{Y}_{max} \frac{S\,Co}{K_sCo + KoS + SCo} \qquad (22)$$

where $\mathcal{Y}$dx/dtx-is the specific microorganism growth rate.

S - the substrate concentration.

Co - partial pressure of oxygen.

Ks and Ko- equilibrium constants.

When analysing experimental data with the help of reciprocal values plots a large dissipation of points was observed that can be explained by the time drift; of activated sludge properties.

As applied to the two-stage substitution mechanism (Equation 22) the time drift causes lowering of all points obtained in the given series of experiments in the ordinate axis by the same value as to the mean statistic value (Vcp) for the given S.

The correction for the time drift (at the investigation of D.O. effect) was defined as a value by which it is necessary to remove the experimental lines along the ordinate axis for the given series of experiments so that they pass through the points corresponding to the mean statistic values of Vcp. that is $\mathcal{A} = Vcp - Vi$ (23)

On the basis of this correction a summar plot was made (1/V = f(1/Co) (Fig. 10) with the help of which the values of constants V_{max} and Ko were determined, characterizing D.O. concentrations effect at various substrate concentrations.

A point with the coordinates $1/V_{max\,cp}$ was plotted on this graph corresponding to the excess substrate concentration (see Fig. 10). A direct line parallel to the other experimental lines passed through it. Intersections of this direct line with the coordinate axises give the reciprocal values of unknown 1/Ko and $1/V_{max}$.

For acetone V max = 133 mg O_2/g/h and Ko = 2.38 mg O_2/l.

The experimental data analysis (see the plot for V = f(Co) in figure 10) has shown their satisfactory agreement with the calculation data according to Equation 22.

A remarkable peculiarity of the dependence obtained is the fact that the greatest effect of D.O. concentration is observed in excess substrate concentration conditions. The role of Co parameter diminishes as the value of S decreases. Hence the maximum increase in the oxidation rate at the expense of D.O. concentration increase is possible when conducting incomplete biological treatment or in initial stages of multi-stage systems.

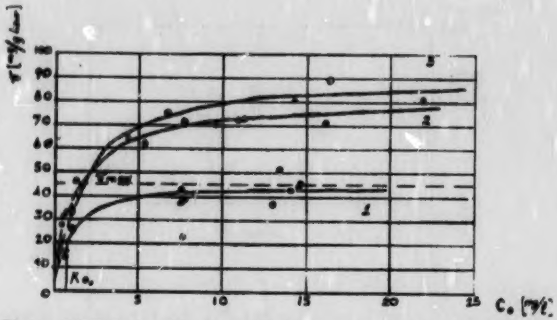


Figure 10 Relationship between the oxygen uptake rate and its convention:
1 - substrate concentration of 94mg/l (COD)
2 - substrate concentration of 360 mg/l
3 - substrate concentration of 450 mg/l

On the basis of Equations 21 and 22 a generalized dependence may be obtained

$$V = V\max \frac{S \cdot Co}{Ks \cdot S + KCo + SCo} \quad \frac{1}{(1 + \gamma x)} \qquad (24)$$

The equation obtained considers the effect of the main components of biochemical oxidation and is used by the authors in mathematic modelling of the biological wastewater treatment process.

D. EFFECT OF THE MATERIAL STRUCTURE ON THE BIOCHEMICAL DESTRUCTION PROCESS

It is rational to analyse the effect of the organics structure on parameters of biochemical treatment using conventional characteristics of the physico-chemical properties of the matter or on the basis of sanitary-chemical analyses. The main data characterizing substances under study and parameters of their biochemical oxidation are given in Table 2. Figure II illustrates the relationship between BOD, COD, specific oxidation rate ρ, the sludge yield volume and the molecular weight of a number of organics tested.

The run of BOD and COD curves (Fig. II) shows that these parameters have the tendency to decrease as the molecular weight grows. This tendency breaks as the structure of the substance changes.

Analysing mutual position of COD and BOD curves one should note that they draw together as the molecular weight grows, that is the BOD/COD ratio increases. Activated sludge growth curve repeats the run of BOD and COD curves in general outline and slightly lowers as the molecular weight of substances grows.

The value of the BOD/COD ratio also gives the possibility for judging about the character of bacterial metabolism responsible for oxidation process.

Catabolic ways of metabolism prevail at large values of this ratio while the anabolic ways prevail at low values. One can judge about this on the basis of the data given in Table 2, from which it is seen that energetic processes prevail over constructive ones at large values of BOD/COD ratio which is followed by low activated sludge yield and low total bacterial number of 1 g of sludge respectively. Constructive processes prevail in processes with relatively low BOD-/COD ratio.

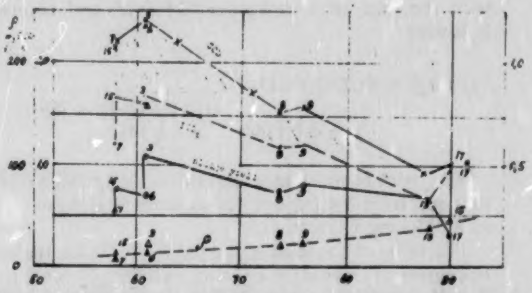


Figure 11 Dependences of BOD, COD of substance, the specific rate of their oxidation and sludge yield on the molecular weight.

This relationship is proved by literary data.

Sharp diminishing of the difference between COD and BOD of 1 mg of the substance as increases claims attention.

This relationship is presented in Figure 12. It must be noted that the growth of with the growth of BOD to COD ratio agrees in outline with the ideas formed.

However, the data about various organics biochemical degradeability have not been systematized yet and enable to make the comparative qualitative evaluations only. In connection with this more detailed analysis of relationship between oxidation rate and BOD/COD ratio is of interest, because the values which form it, are accessible for quantitative determinations with the use of standard methods.

In Table 2 the data are given about BOD and COD of particular substances and about specific rates of their oxidation. In general these data are obtained as a result of laboratory investigations carried out at the Institute VODGEO.

Graphical forms of the following functions are constructed for the analysis of these data:

$$\rho = f\,(COD\text{-}BOD); \rho = f\left(\frac{BOD}{COD}\right);$$

$$\rho = f\,(C).$$

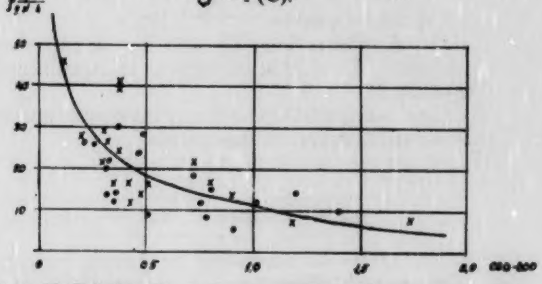


Figure 12 Relationship between specific oxidation rate and COD-BOD difference
x - according to VODGEO data
o - according to construction norms and laws II. 74.

where C is a specific amount of organic carbon in a tested substance expressed in g of C/g of substance.

It follows from here that despite the essential dissipation of experimental points correlation between the rate of oxidation and BOD/COD and COD-BOD values is followed rather clearly.

Statistic analysis of the experimental data was carried on with the help of a computer "M P-2" and showed the following:

1) for $\rho = f(\text{COD-BOD}) = \dfrac{1}{[a(\text{COD-BOD}) + B]^2}$ (25)

a = 0.1164 b + 0.1427.

The root-mean-square deviation (dispersion) of this function from the majority of experimental points is equal to 8.9350 mg O_2/g/hour.

The value of confidence interval E = 0.2262 at the number of degrees of freedom K equal to number of points n = 42 is K = n -1 = 41.

The value of confidence of probability is equal to 0.96 (significance level is 28%).

2) for the dependence of the type

$$\rho = f\left(\frac{\text{BOD}}{\text{COD}}\right) = \frac{1}{\left[a\left(\frac{\text{BOD}}{\text{COD}}\right) + B\right]^2} \qquad (26)$$

a = 0.002898 b = 0.4421

The value of confidence interval E = 0.1510. The root-mean-square ratio of approximating function

$$\sigma = 11.4548 \frac{\text{mgO}_2}{\text{g/hour}}$$

Confidence probability P = 0.87 at the number of point equal to 42.

Thus for practical evaluations the following dependence providing more close correlation of parameters may be recommended:

$$\rho = \frac{1}{/0.1164\,(\text{COD-BOD}) + 0.1427/^2} \qquad (27)$$

The dependence BOD = f(C) (Fig. 13) is described by the straight line equation y = ax + b, where y = BOD, a = 4.7579, b = 1.1894, that is BOD = 4.76 • C - 1.19. (28)

The total dispersion = 0.58195.

The confidence interval value E = 0.3142. Confidence probability P = 0.99 at the number of experimental points equal to 21.

Substituting BOD value from Equation 28 into Equation 27 we shall obtain the dependence

$$= \frac{1}{0.1164\,[\text{COD}-(4.76 \cdot C - 1.19)] + 0.1427^{\;2}} \qquad (29)$$

which allows to determine the specific oxidation rate without the BOD analysis.

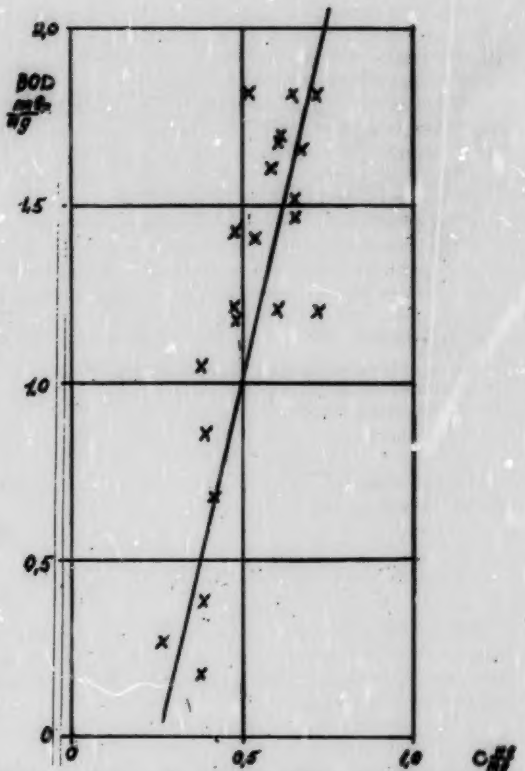


Figure 13 Relationship between BOD and dissolved carbon concentration.

While evaluating the accuracy of obtained dependences it must be born in mind that the reproducibility of experiments run for determination of biochemical oxidation rate is comparatively poor; BOD and COD values are not absolutely accurate either.

In the experiments run for determination of specific oxidation rate ( ) the deviation from mean values may exceed 50%; in the analysis for BOD total this error varies within the limit of ±10%. The COD value is defined more accurately but in this case the deviations from mean values within the limit ±5% are the most probable. With the ratio caused by errors of the experiment and the analysis taken into account the relationship between COD and BOD is more trustworthy.

The relationships obtained (27, 28, 29) are valid for pure substances and their applicability to complex mixtures characteristic of industrial wastewaters demands further development. The methodical approach to the problem still demands the further development. Apparently, the results of this problem's solution cannot be obtained soon, but for practical purposes the use of approximated relationships is possible.

The experimental data analysis has shown also that the correlation between V max and BOD/COD is observed (Figure 14). It is interesting to note that the experimental points formed two straight lines each of them is characterized by the value $\dfrac{\text{COD}}{\text{C}}$

Dependence of constants Ks and on V max is given in the plot (Figure 15). A rather clear dependence of on V max can be seen here, but as far as the constant K is referred the tendency for its increase as the V max decreases can be marked. This aspect alongside with the relationship between the biomass yield and substrate properties demands the further researches.

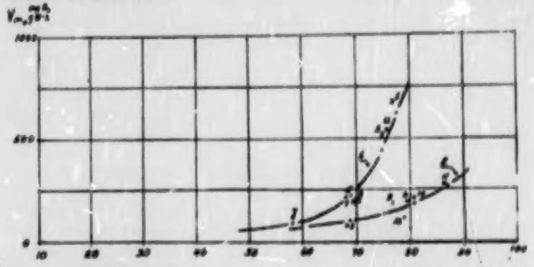


Figure 14 Relationship between the maximum oxidation rate Vm and BOD/COD ratio.
1 - at COD/C = 3.6 - 4.1;2 - at COD/C = 2.2 - 3.3.

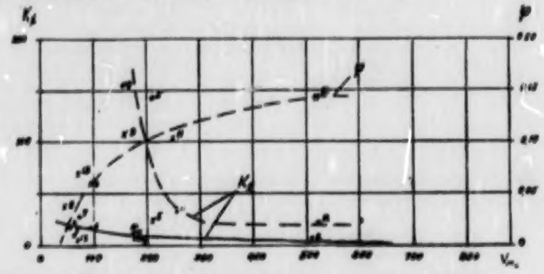


Figure 15 Relationship between Ks and constants and Vmo.

Conclusions

Investigations into biological treatment kinetics carried out under laboratory conditions drew the following conclusions:

1. Evaluation of the subject under consideration dynamic properties is of great importance when choosing the methods of investigation.

Researches with the so-called "sharp" tests run in batch conditions are appropriate to be carried on during investigations of slow inertial processes. During the study of the processes with high inertia dealing with microorganisms acclimatization the continuous-flow cultivation method should be used.

2. The peculiarity of the experiments with activated sludge is the poor reproducibility of the results due to the time drift of activated sludge biochemical properties. This should be taken into account in carrying out the experiments and analysing the data obtained.

3. For investigations of the kinetics of low inertial processes connected with the effect of substrate, D.O., activated sludge concentrations and pH, temperature etc, it is appropriate to use manometric methods.

. Special kinds of instruments - respirometers - based on this principle permit to run the experiments in a wide variation range of parameters.

4. It is proved experimentally that the effect of substrate concentration on the biological treatment rate may be described by the Michaelis - Menten Equation. The effect of MLVSS upon the rate of biological treatment is described by the Ierusalimsky Equation taking account of the process inhibition by products of metabolism.

5. The joint effect of substrate and D.O. concentrations is described quite satisfactorily by the equation of a bisubstrate reaction proceeding in accordance with the two-stage enzyme substitution.

6. The generalized kinetic equation was obtained permitting the effect of the biochemical oxidation main components to be objectively taken into account.

7. Increase in the number of carbon atoms in the molecule of substance causes decrease in the biochemical oxidation rate and intensification of biological synthesis processes aliphatic alcohols serve as the example of this phenomenon.

The various functional groups available and their position in the molecule of substances produce an important effect on the process kinetics.

The oxidation rate of izoalcohols is lower than that of alcohols with normal structure. Biological degradability of isoalcohols decreases from primary alcohol to the tertiary one.

When the number of carbon atoms in the molecule is the same and the various functional groups determining the chemical properties are available, the highest destruction rate is observed in normal alcohols and organic acids.

8. The analysis of literary and experimental data obtained have shown that the relationship between the rate of oxidation and molecular weight is very contradictory.

The most satisfactory correlation for individual substances is being observed between the specific rate of oxidation and the difference between COD and BOD as well as between and COD-carbon difference. Relationships obtained as a result of statistical handling (27, 29) allow us to define the specific rates of oxidation for individual substances.

The applicability of these relationships to the multicomponent substrates needs to be experimentally verified.

Chemical Additions to Biological Treatment of Petroleum Refinery Wastewater

Allen Cywin[*]
U.S.E.P.A.

Introduction

The form contaminants take in petroleum refining effluents is very important to the design and operation of end-of-pipe treatment facilities and include suspended, colloidal and soluble materials. In the raw waste loads, most BOD and COD frequently occurs as suspended and colloidal matter. Certainly, gross quantities of contamination tend to exist as colloidal and suspended matter, whereas variability of soluble components is much more limited. Therefore destabilization and chemical removal of colloidal and suspended matter in a chemical pretreatment step substantially lowers and equalizes contaminant levels prior to secondary treatment. This of course leads to savings in costs and energy in biological treatment.

Table I provides an overview of various treatment processes that may be employed in producing an effluent of drinking water quality from petroleum refinery wastes.

The use of chemical systems for treating specific petrochemical wastes, as an addition to biological treatment, has been successfully employed. The most common methods for chemically treating petrochemical wastes include neutralization, precipitation, coagulation, and oxidation, illustrated under the "Intermediate Treatment" sequence of Table 1. (1) (2)

Pre- and primary treatment may be required to remove certain materials which would adversely affect the biological system. Oils are difficult for the organisms to metabolize due to their low solubility. Inorganic and non-biodegradable organic suspended solids will tend to build up in a treatment system, decreasing the proportion of active biological solids, and thus adversely affecting the treatment efficiency. Sulfides react with dissolved oxygen and reduce the oxygen available to the organisms. Heavy metals are toxic at defined concentrations and must be removed or reduced to safe levels. Also, waste streams with potentially toxic organic compounds should be separated and treated prior to treating in a biological system.

Sequence	Treatment	Processes	Objectives
Primary treatment	1. Removal of gross amounts of hydrocarbons and solids	Primary API separators	Removal of free oil and solids
Intermediate treatment	2. pH control	Mixing and neutralization	Adjust pH to proper range for subsequent treatment by immediate oxygen demand (IOD) reduction, filtration and ASP operation in nitrification mode
	3. Immediate oxygen demand (IOD) reduction	Aeration and mixing	To reduce immediate oxygen demand and peak concentrations of contaminants by air oxidation and equalization in a series of basins
	4. Removal of colloidally dispersed phase	Chemical coagulation and filtration	To reduce oil, biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Removal of oil makes ASP more operable in desired mode.
Secondary	5. Dissolved organics and ammonia removal	Completely mixed activated sludge process	To maximize removal of ammonia and BOD, COD causing substances.
Tertiary	6. Phase removal	Filtration	To maximize effluent quality by removing suspended solids and their associated BOD, COD and threshold odor causing substances.

Chemical Treatment

Neutralization and pH Adjustment - Neutralization of petrochemical wastes may be desired for several reasons, including:

a) preparation of a waste for biological treatment,
b) preparation of a waste for direct discharge,
c) pretreatment for efficient coagulation,
d) prevention of attack and corrosion of conveyance or process equipment, and
e) prevention of unwanted precipitation of waste components.

Neutralization implies the adjustment of a wastewater pH to values at or near neutral pH; i.e., pH seven. (However, most petroleum refinery biological treatment systems operate efficiently at pH 6-8.) Types of wastes generally neutralized are (a) dilute acid or alkaline wash waters; (b) spent caustics; (c) acid sludges from alkylation, sulfonation, sulfation, and acid treating processes; and (d) spent acid catalysts (3).

Acid streams can be neutralized by mixing the waste with lime slurries, or by adding caustic soda (NaOH) or soda ash (Na_2CO_3). Limestone beds ($CaCO_3$) are occasionally used,

---

[*] Senior Science Advisor, Office of Water & Hazardous Materials

Presented at the Third U.S./USSR Symposium for waste water treatment and control at Moscow, USSR, August 23-25, 1976.

either as an upflow system or a downflow system.

Sulfuric acid (H_2SO_4) is the most common neutralizing agent used to neutralize spent caustic wastes, although hydrochloric (HCl) can also be used. Acid sludges are normally hydrolyzed to free acids prior to their use as neutralizing agents. Spent caustic neutralization with an acid can be designed as a batch or a continuous system. The carbon dioxide in flue gases can also be used to neutralize spent caustic solutions. Flue gas neutralization is economically feasible provided that the gases are available at high enough pressures so that no compressor is required to inject them into the spent caustic solution. It neutralizes alkaline wastes by the forming of a weak carbonic acid. Spent acid catalyst and sludges have been spread in pits filled with lime, limestone, or oyster shells for neutralization. It should be noted that pH adjustment is commonly used to facilitate coagulation and precipitation.

Coagulation - Precipitation - The addition of coagulants under proper conditions causes the formation of a settleable precipitate containing waste materials which can be removed by conventional sedimentation or flotation processes. It should be noted that coagulation is always followed by some type of solids-separation process. The most commonly used coagulants are hydrated aluminum sulfate (alum), ferrous sulfate, and ferric salts. The conventional coagulation system utilizes a rapid mix tank followed by slow agitation of the mixture to promote growth of floc particles which settle. The sludge-blanket clarifier, which provides mixing, flocculation, and settling in the same unit, has had many industrial applications because of its compact dimensions.

Coagulant aids are sometimes necessary to promote bridging between floc particles and render the floc more settleable. The most common coagulant aids are activated silica, bentonite clays, the organic polyelectrolytes, and water treatment clarifier sludge. The three types of polyelectrolytes are categorized by their electrochemical nature, specifically, cationic, anionic, and nonionic.

Organic polyelectrolytes are helpful in improving the effectiveness of the air flotation process and in obtaining a high degree of clarification. In many plants organic emulsion breakers have replaced traditional alum treatments.

Besides yielding a better quality effluent, organic emulsion breaker programs, by reducing the dosage of inorganic chemicals, can also reduce the amount of sludge generated by 50-75%. A significant saving in further sludge treatment, or truckout, can be realized because the sludge resulting from the organic polyelectrolyte treatment contains at least as much oil as in the inorganic sludges, but in a much smaller volume. Plants that incinerate sludge have realized a higher value (Btu per pound) with the organic sludge.

Provisions must be made for the disposal of the sludges formed by the settled precipitates from coagulation-precipitation processes. Landfills are the most common form of inorganic sludge disposal, while organic sludges are usually dewatered by some filtration method and subsequently incinerated or buried.

High molecular weight cationic polyacrylamide flocculants produce efficiencies in sludge dewatering processes.

Figure 1 illustrates in simple form the use of polyelectrolytes at other points in the biological process where emulsion breakers may enhance the system.

These are usually applied after jar and/or pilot tests determine which of the many polyelectrolytes available will be most efficient. For high-rate and extended aeration systems (F/M ratios $>.6$ + $<.2$, respectively) cationic "polyamine" coagulants often work best. For conventional aeration (F/M ratios 0.2 - 0.6) systems polyacrylamide cationic coagulants are often preferred, as illustrated in Figure 2.

A full comparison of an acid-alum-lime treatment system and an organic polyelectrolyte emulsion breakers program shows these advantages for the organic system:

(a) lower total dissolved solids in the effluent for plant reuse;
(b) elimination of final clarification and lime or caustic neutralization; and
(c) reduction in corrosion rates, alum usage, and sludge generation.

Oxidation processes - Oxidation processes are used to treat both organic and inorganic contaminants using oxygen or other chemicals as the oxidizing agents. The oxidation of sulfides to sulfates using steam and air is an effective treatment method; however, wastes containing high concentrations of phenol cannot be treated in this manner because phenols interfere with sulfide oxidation. If large quantities of mercaptans or mercaptides are present in the waste, a reoxidizer may be required to insure complete oxidation.

Catalytic oxidation is usually applied when the fuel value of a waste is too low for conventional incineration. The process was originally designed to operate in the vapor phase but has been successfully applied to aqueous wastes. Laboratory studies have shown that dilute aqueous organic wastes could be effectively oxidized at temperatures below 600°C by using a copper-chromate catalyst. Investigations have demonstrated that hydrocarbons also could be oxidized by using metal oxide catalysts. The initial cost of catalytic oxidation units may be 20 to 30 percent greater than that for conventional incinerators, but for dilute organic wastes the operating costs may be 15 to 20 percent less.

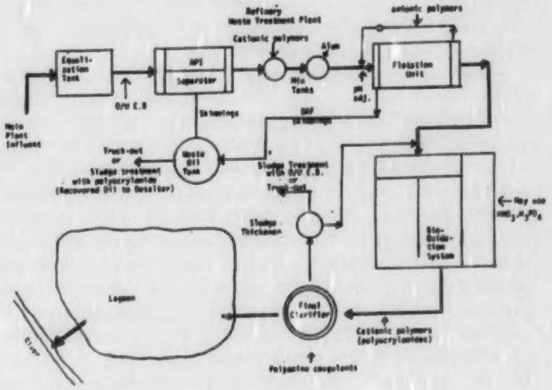


Figure 1

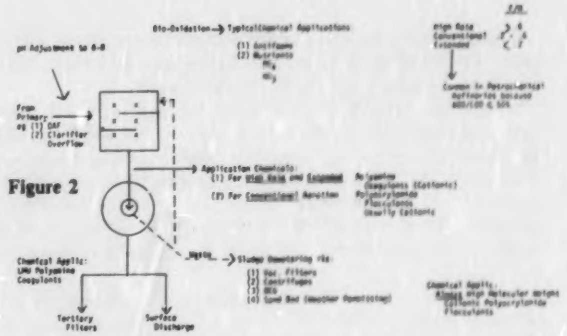

pH Adjustment to 6-8
Bio-Oxidation → Typical Chemical Applications
(1) Antifoams
(2) Nutrients
From Primary eg (1) DAF (2) Clarifier Overflow
High Rate
Conventional
Extended
Application Chemicals:
(1) For High Rate and Extended
Polyamine Coagulants (Cationic)
(2) For Conventional Aeration
Polyacrylamide Flocculants Usually Cationic
Waste
Sludge Dewatering via:
(1) Vac. Filters
(2) Centrifuges
(4) Sand Bed (Weather Permitting)
Chemical Applic: LMW Polyamine Coagulants
Tertiary Filters
Surface Discharge
Chemical Applic: Always High Molecular Weight Cationic Polyacrylamide Flocculants

Figure 2

Chlorine (C_1) has been used successfully to oxidize phenol and cyanide in petrochemical wastes. The oxidation of phenols must be carried to completion to prevent the release of chlorophenols which cause objectionable tastes and odors in drinking water. Cyanides can be oxidized to carbon dioxide and nitrogen by chlorination if the pH is maintained in excess of 8.5 and sufficient chloride used, thus preventing the release of toxic cyanogen chloride. Chloride dioxide has been shown to overcome these and other disadvantages of chlorine and hypochlorite oxidation, although this treatment is very expensive.

Ozone (O_3) has been proposed as an oxidizing agent for phenols, cyanides and other unsaturated organics because it is a considerably stronger oxidizing agent than chlorine. The chief disadvantage in the United States is the high initial cost of ozone generation equipment, although there seems to be more experience in the USSR (for drinking water) where the costs may be different. Ozone has several advantages, one of which is its ability to react rapidly with phenols and cyanide.

Miscellaneous Methods - Ion exchange has been used to remove specific petrochemical pollutants. Quaternary ammonium anion resins have successfully removed phenols in the laboratory.

A full scale demonstration of a chemical-biological treatment of petroleum refinery waste water has been completed. The results of recent E.P.A. sponsored research investigations (4) of the AMOCO company's Yorktown refinery waste lagoon effluent and API separator effluent to determine the applicability of coagulation/mixed-media filtration on these streams illustrates the efficiency of combining these techniques. This relates to step 4 of Table 1 (removal of colloidal material).

Coagulation/mixed-media filtration - Mechanisms for retention of solids within pores of filter media may be separated into two principal processes: a transport step and an attachment step. The transport step involves movement of the dispersed phase material to the vicinity of the filter media surface, and the attachment step involves attachment of the particles on the media surface. The transport mechanisms may involve diffusion, interception, sedimentation and hydrodynamic actions. The attachment mechanisms may involve van der Waal forces, electrical double layer interaction, mutual adsorption or hydrogen bonding or ionic forces. Experimental comparisons of the filtration of colloidal, ferric hydroxide suspensions with the filtration of well flocculated suspensions of ferric hydroxide, both performed under identical conditions of filtration, demonstrate a much higher filtration efficiency for the floc. Studies have shown that removal of colloidal suspensions by filtration appears to be possible only when the colloidal particles to be filtered carry an electro-kinetic charge opposite to the charge of the filter media used. The removal of the colloid is by electro-kinetic sorption of the colloidal particles on the surface of the filter media. This kind of "filtration" phenomena seems to have limited application to the filtration of industrial waste water because of complications encountered in application, the complexity of which are beyond the scope of this paper.

Colloidal Destabilization - In most cases, the application of filtration to petroleum refining waste waters will not be optimized unless the colloidal material in suspension is destabilized by essentially neutralizing the surface charge on the colloids. The neutralization of the charge using conventional primary coagulants is simple, but must recognize the condition of the water. Overdosing with alum, for example, can be a most deleterious response to a direct filtration system that is not performing satisfactorily.

Stumm and O'Melia (5) describe the equilibrium composition of solutions in contact with precipitated primary coagulants in the interesting manner shown in Figures 3 and 4. These diagrams are calculated using equilibrium constants for solubility and hydrolysis equilibria. The shaded areas A and B in each figure are approximate operation regions for air flotation and clarifiers (region A) and direct filtration (region B). Both regions are assumed to cover a pH range of 6.0 to 8.5. The coagulant dosage ranges from 33 to 200 mg/l in region A and 3.3 to 20 mg/l in region B. These figures are useful in the interpretation of some filtration results.

With reference to Figure 4, the isoelectric point for ferric hydroxide coincides with the region of minimum solubility, and operating regions for water treating (destabilization) always yield a hydrolyzed primary coagulant with a desirable, positive, zeta potential.

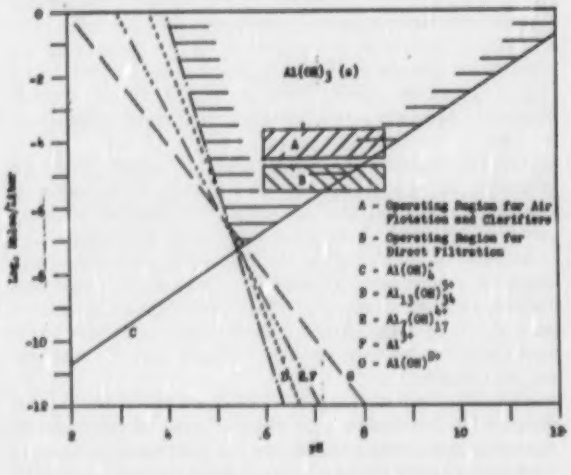


Figure 3 Equilibrium compositions of solutions in contact with $Al(OH)_3$

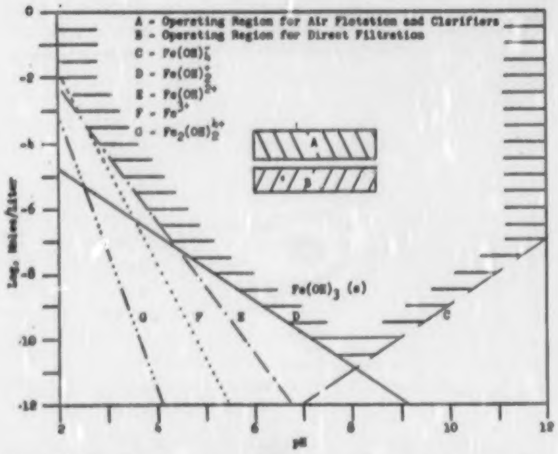


Figure 4. Equilibrium compositions of solutions in contact with $Fe(OH)_3$

In many refinery situations, however, it is difficult to use this desirable condition because the presence of sulfides and strongly reducing conditions cause the reduction of ferric to ferrous iron and the formation of mixed iron sulfides with no coagulation powers. In fact, in some refinery waters the use of iron coagulants at modest dosages may contribute to stabilizing solids rather than destabilizing them.

While alum has no redox or sulfide chemistry comparable to iron, its amphoterism and solubility pose definite limitations on alum usage. With reference to Figure 3, a substantial portion of operating region B lies in the area where alum is soluble and the predominant equilibrium species is negative, $Al(OH)_4^-$. In the more acidic part of region B, however, the concentration of equilibrium ionic species is very much lower and much less negative. Considering these data, it is not unexpected that investigators consistently report optimal coagulation/flocculation results with alum at a pH of 5-6.

With inspection of Figure 3, one may question why alum is effective at all for neutralizing negatively charged colloids in the indicated operating regions. One approach to explaining observed performance requires understanding that the data in Figure 3 are equilibrium data; but before equilibrium is reached, substantially different conditions exist.

Alum very readily hydrolyzes to form polymers in a complex manner not well defined. The hydrolytic pathway and reaction rates are affected by pH, temperature, other ions, etc. The hydrolytic reactions are not instantaneous, and as they proceed, positively charged hydroxo polymers are formed which are available for colloid adsorption. The hydrolyzed species have enhanced adsorption capabilities possibly due to larger size, less hydration, and the presence of coordinated hydroxide groups. In solutions more alkaline than the isoelectric point, the positively charged polymers are transient and, at equilibrium, anionic polymers prevail. In modestly alkaline solutions, the transient, positively charged polymers appear to contribute to destabilization of colloids. On the other hand, in solutions more acidic than the isoelectric point, the positively charged polymers prevail at equilibrium and destabilization of colloids is achieved at significantly lower coagulation treatment levels.

While coagulation/flocculation of refinery waste water can frequently be achieved over a wide pH range using primary coagulants supplemented with polyelectrolytes, typically there is a very definite optimal pH that may simplify, or even be required by, direct filtration. Operating at the optimal pH yields benefits of maximum removal of discontinuous phase material with minimal coagulant requirement and sludge generation.

Frequently, refinery waste waters only require 5 to 10 mg/l of primary coagulant at a pH range of 6 to achieve destabilization for filtration. When this level of chemical treatment is observed in jar tests, the coagulant dosage may be much below that required for generation of floc; however, excellent filtration results are achieved. The destabilized particles penetrate into the pores of the filter media, the media aids the flocculation process, and the particles are effectively trapped with high solids loadings. Too much primary coagulant can be added at a pH of 6 and some suspended matter restabilized. Too much coagulant puts an unnecessarily heavy solids burden on the filter and the result is rapidly increasing pressure drops, early breakthrough and excess backwash sludge to handle.

At a pH of 8, substantially more primary coagulant may be needed to neutralize the zeta potential. The dosage may be 30 mg/l or more with the generation of a substantial floc size instead of the almost invisible pin-point floc of suspensions successfully filtered at a pH of 6. The more voluminous floc does not penetrate into the filter media as well as does the pin-point floc and lower solids loading, higher pressure drops, and more chemical usage, backwash and sludge volumes result.

At a pH of 9, the zeta potential of the system may never be neutralized and, of course, is not optimal as such for direct filtration. With iron salts, chemical coagulation/flocculation at a pH of 9 or more can yield superb results with some waters, but a different clarification mechanism is involved. Comparatively large dosages of coagulant are used which generate large, voluminous floc particles that trap and enmesh the suspended matter in the water being treated and retain the solids in the sludge blanket. This approach is not optimal for direct filtration but requires pretreatment in a clarifier to handle the voluminous sludge volume generated. The clarifier water is then polished by filtration using polyelectrolytes to destabilize the residual suspended matter.

Figure 5 illustrates the effect of treating a refinery effluent water with fixed levels of overdosage, underdosage, and optimal dosage of primary coagulant at various pH levels. For this example, the optimal dosage is defined as the coagulant required to bring the zeta potential of the system into the target zeta potential range of ±5 mV necessary for destabilization of the suspended matter preparatory to direct filtration. To emphasize the importance of pH for these systems of over, under, and optimal treating with coagulant, there is a pH range where the system is destabilized and receptive to clarification by direct filtration.

For the optimal dosage in curve A, the system is destabilized over the widest pH range of 5.5 to 8.4. Underdosing (curve C) provides a destabilized system for filtration only at a pH of about 6.5 or less. Overdosing (curve B) results in the narrowest pH range for effective destabilization of about 0.6 pH units, i.e., 7.65 to 8.25.

Refinery effluent waters may vary rapidly in pH over a short time span which makes it desirable to determine the optimal coagulant-pH balance. Frequently, poor or no pH control is available. In these cases, the destabilization of suspended matter frequently can be "desensitized" to pH somewhat by using coagulant/polyelectrolyte combinations. The preferred operating procedure that frequently makes the filtration system essentially free from upset is a two chemical system: a primary coagulant supplemented by a polyelectrolyte. Two cases seem appropriate: 1) For the operating range of 6-9 pH, an underdosage of primary coagulant is used and is supplemented by addition of a cationic polyelectrolyte. This combination of chemicals broadens the effective pH range of destabilization of curve C in Figure 5, and, additionally, the chemical properties more adherent to the filter media. 2) For the operating range of 5-7 pH, the polyelectrolyte used to supplement the primary coagulant may be a non-ionic or very weakly anionic. The non-ionic or very weakly anionic polyelectrolyte is useful in systems that tend to modest overdosage situations with primary coagulant. Massive overdosing with primary coagulant can be compensated for somewhat by non-ionic or very weakly anionic polyelectrolytes but rapidly blind the filter. These chemical treatments are also useful when high hydraulic loadings are applied to the filter or rapid rate increases occur, both of which may tend to redisperse trapped solids and cause premature breakthrough.

Strong, or very strong, anionic polymers usually perform the poorest in tests comparing cationic, non-ionic, very weakly anionic, weakly anionic, fairly strong anionic, strongly anionic, and very strongly anionic polyelectrolytes. In one instance, treatment with only a cationic polyelectrolyte at a less than 1 ppm outperformed all other combinations of chemical treatment for destabilization of suspended matter preparatory to filtration.

Another distinction that may be important is the nature of the colloids to be destabilized: inert materials including clays, silica, coke fines, oil particles, etc., or biocolloids consisting chiefly of bacteria. Amoco's (4) work on colloid destabilization at other refineries has been largely on inerts, or a mixture of colloids predominately inerts with some biocolloids. The work of McLellon et al. (6) and Stumm et al (5) indicates that where principally biocolloids are concerned, stability is less dependent on repulsive electrostatic interactions and relates primarily to the interaction of the hydrophilic surface of the biocolloid with the aqueous solvent. The source of colloid surface charge is through acid-base interactions of ionogenic functional groups. The authors cited conclude that aggregation of biocolloids is by chemical interaction of the hydroxy metallic polymers with the ionogenic groups of the colloid followed by chemical bridging. If the destabilization mechanism for biocolloids is such a special case, the chemical pretreatment may be optimized by emphasizing the use of organic polymers known to form chemical bridges. The optimal chemical pretreatment would then be expected to be a multichemical system.

Tests indicate that in warm brackish water a two-chemical system at low concentrations was satisfactory whereas for cold brackish water a three chemical system at higher concentrations may be required.

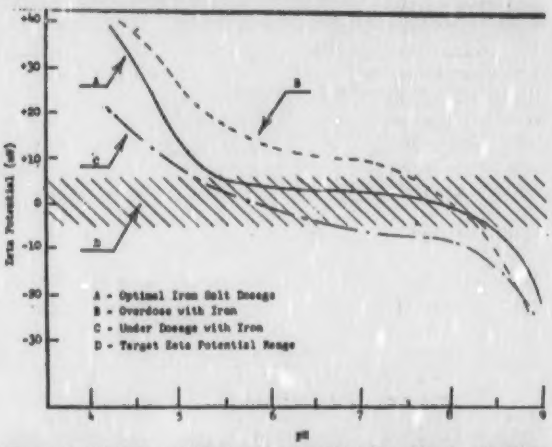


Figure 5. Variation of final zeta potential with pH when treating refinery effluent having negative zeta potential with three levels of coagulant dosage

Polyelectrolytes screened vary widely in effectiveness, and optimizing chemical pretreatment involves testing a series of commercial polyelectrolytes at various combinations until an optimal combination was found (7)

1. Two Chemical Systems
   a) Optimize pH.
   b) Use a primary coagulant plus an organic cationic polyelectrolyte, or
   c) Use a primary coagulant plus an organic non-ionic or weakly anionic polyelectrolyte.
2. Three Chemical Systems
   a) Optimize pH.
   b) Use a primary coagulant/organic cationic polyelectrolyte/weakly anionic polyelectrolyte treatment sequence.

Nutrients - Effective biological treatment of any organic contaminant requires the availability of essential nutrients for the organism. The mineral nutrients required by bacteria are available in sufficient amounts in most wastewaters, but nitrogen and phosphorus requirements are more critical and many petrochemical wastes are deficient in one or both of these elements. Nitrogen (N) and phosphorus (P) requirements for biological treatment have been related to the magnitude of the degradable organic content of wastewater as represented by BOD. Generally, a BOD:N:P ratio of 100:5:1 will provide sufficient amounts of these nutrients. Nitrogen is most readily available in its reduced form as ammonia, ammonium ion, or amino nitrogen. Organic nitrogen, nitrates, nitrites, and organic compounds containing these forms can also be used, but a considerable expenditure of energy is required to reduce these forms to ammonia nitrogen. Phosphorus is usually added in the form of phosphoric acid or soluble phosphorus salts since they are most readily assimilable.

Summary

In summary, biological treatment is the key end-of-pipe element in the overall treatment systems, for petroleum refinery wastes. Therefore the unit processes within the treatment system should be optimized to utilize the biological process for removal of soluble contaminants. In the United States we have learned that the use of chemical pretreatment as well as other physical processes (such as dissolved air flotation and mixed media filtration) will enhance the performance of the biological systems by removing colloidal and suspended matter. This not only improved the efficiency of the biological treatment process but saves on cost of equipment and operations.

References

1. Grutch, J.F. and Mallatt, R.C., *Optimize the Effluent System*, Hydrocarbon Processing (March 1976)
2. Lacy, W.J. and Cywin, Allen, *Physical-Chemical Treatment of Wastewaters from the Petroleum Refining - Petrochemical Industry* Joint U.S. - USSR Symposium, Cincinnati, Ohio (November 1975)
3. Halper, Martin and Cywin, Allen, *Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Petroleum Refining Point Source Category*, Environmental Protection Agency, EPA - 440/1-74-014-1, (April 1974)
4. Grutch, J.F., Mallatt, R.C., and Peters, A.W., *Chemical Coagulation/Mixed-Media Filtration of Aerated Lagoon Effluent*, EPA - 660/2-75-025, (June 1975)
5. Stumm, W. and O'Melia, C.R., *Stoichiometry of Coagulations*, Jour. AWWA 60:514 (1968)
6. McLellon, W.M., Kernath, T.M. and Chao, C., *Coagulation of Colloidal and Solution Phase Impurities in Trickling Filter Effluent*, Jour. WPCF, 60(1):77-91, (1972)
7. Surchek, J.G., and Tutein, T.R., *Simplified Method Determines Cost Performance of Polymeric Flocculants*, Water and Sewage Works (January 1976)

MINISTRY OF HIGHER AND
VOCATIONAL SECONDARY
EDUCATION OF THE USSR
LENINGRAD INSTITUTE OF CIVIL
ENGINEERING

S.M. Shifrin, B.G. Mishookov, G.V. Ivanov,
E.K.Goloobovskaya

The Trends in Intensification in Biochemical Treatment of High Density Wastewater

Intensification of biochemical treatment of waste water which has high density of organic matter may be carried out in a number of ways, the major ones being the following:

—increase in load imposed on microbial mass by establishing the optimum conditions for activated sludge behavior;

—usage of high density activated sludge;

—usage of thermophilic activated sludge.

The first trend is implemented by increasing the density of microorganisms and reducing the retention period of liquid inside the aeration tanks. When the density of microorganisms increases, the rate of their removal goes up; the relation between the treatment rate and the increase in density of microorganisms is of non-uniform nature. Fig 1 shows an example of dependence (which has been established by us) of treatment rate on the density of microorganisms in sludge-liquid mixture in the aeration tanks with the oxidation (under contact conditions of organic matter in the influent coming from the food industry enterprises.

The dependence of treatment rate on the organic matter density is of S-shaped form and somewhat differs from well-known patterns established by Michaelis-Menton; Monod and others.

In general the rate of treatment may be represented as an equation of trimolecular reaction

$$r = \frac{dC}{dt} = -K\ (C)^n\ (D)^m\ (O)^p \qquad (1)$$

where C,D,O - respectively, densities and concentration of organic matter, activated sludge and dissolved oxygen in the liquid;

K - the constant value of the reaction rate;

n,m,p - empirical values.

It is generally accepted that dissolved oxygen concentration in excess of 0.5-1.0 mg/l is of little practical significance for the biochemical treatment rate, provided the mass-transfer of oxygen is not connected (as is the case in diffused aeration systems, for example with the speed of agitation of sludge-liquid mixture.) If the oxygen concentration and the speed of agitation related to it do not restrict the treatment rate, then the formula (1) turns into an equation of bimolecular reaction. Within the wide range of concentration changes the values of "n" and "m" are the variables. The value of "n" ranges from 2 to 0.5 with little and medium loads on activated sludge and is reduced to zero when the load increases. The value of "m" is frequently assumed to be the constant (in case of narrow ranges of changes of "D" value), although in general "m" decreases when "D" increases. One can compare the efficiencies of treatment only on the basis of rate "r" as with the changes of "n" and "m", the value of "K" becomes incomparable. In view of this it is advisable to apply the first criterion of Damkohler

$$Da_I \qquad Da_I = \frac{r \cdot l}{v \cdot c} \qquad (2)$$

Where r - Treatment rate;
l - determining linear characteristic;
v - determining velocity of liquid movement;
c - concentration of matter going into reaction.

When applying this criterion to wastewater biochemical treatment it is possible to change the criterion somehow taking into account the equation (1):

$$Da_I \quad \bullet \quad \frac{kC^nD^mO^p}{vC} = kC^{n-1}D^mO^pt \qquad (3)$$

Damkohler's modified criterion under the equation (3) enables to compare efficiencies of treatment of a specific kind of wastewater while changing the organic matter density (C), the activated sludge dosage (D) and the aeration duration.

The way the treatment rate changes (Fig. 1) indicates that usage of one-stage facilities is not advisable since the treatment average rate in such facilities turns out to be low.

Treatment in two-stage or three-stage aeration facilities in which the optimum conditions for existence of specific activated sludge are provided is economically more preferable. On the basis of our research one may come to the conclusion that the two-stage treatment is applicable with the organic matter density of up to 8.0 - 12.0 g/l (calculated at the bichromate COD), while the three-stage treatment is advisable when the density calculated at the COD is within 10.0 - 15.0 g/l. It should be borne in mind that we are dealing here with the organic matter which undergoes oxidation without great difficulties during the biochemical treatment (wastewater from the food industry enterprises, influent from live-stock farms etc.) The establishment of optimum conditions for activated sludge existence in each stage of aeration facilities provides for the proper speed of agitation and supply of dissolved oxygen. In the first stage of aeration facilities the proper agitation and dissolved oxygen supply is achieved with the electric power consumption of up to 100 watt/hour per $1m^3$ of volume, in the second stage - up to 70 watt/h/m^3, in the third stage - up to 50 watt/hM^3 (these power consumptions hold good for the aeration facilites with the capacity of 150-500 m^3). Dissolved oxygen is contained in the liquid at a level of 0.1-0.5 mg/l in the first stage; 2.0-3.0 mg/l in the second stage; 3.0-4.0 mg/l in the third stage. Nitrification was observed in the second and third stages. The third stage usually acts as an aeration-nitrification tank and at the same time it acts as a preventive means to hold up the microbial mass which is periodically entrained by the effluent from the second stage.

The organic matter oxidation rate amounts to 200-300 g/hour of COD per 1 m^3 of volume of the first stage aeration tank, 100-150 g/m^3/h in the second stage, 10-30 g/m^3/hour in the third stage, while the treatment efficiency makes up approximately 50,80 - 90,95 - 97% of COD respectively after the first, second and third stages of aeration tanks.

The second trend in stepping up the treatment provides for an increase in density of microbial mass in the facilities (higher density of activated sludge). The increase in the microbial mass volume results in the reduction of specific velocity of organic matter removal per unit weight of microorganisms. At first sight higher density of activated sludge does not yield an anticipated result. However, it should be borne in mind that activated sludge of higher density has considerable constance and is able to withstand drastic changes in density with comparative ease, which is typical of the high density wastewater. Higher density of activated sludge is achieved through employment of intensive means of microbial mass separation - by filtration, flotation and prolonged settling. But not all these means are applicable to hold up the microorganisms after the first stage of aeration facilities. High rate treatment in the first stage generates the microbial mass consisting of very fine, badly flocculating particles, so that the holding up of this mass is a rather complicated problem. The sedimentation properties of microbial mass are influenced positively by the inert solids in the form of specially introduced medium, such as activated carbon, or in the form of suspended matters contained in wastewater. In view of the current practice of microbial mass separation the prolonged one-stage or two-stage settling proves to be the least expensive and the most feasible one.

In the multi-stage aero-accelators designed for treating live-stock farm wastewater the activated sludge density was maintained equal to 10-18 g/l in the first and second stages and 6.0-8.0 g/l in the third stage. The influence of the activated sludge density on rate and efficiency of treatment comes to be observed when the density is reduced to 6.0-8.0 g/l. After the microbial mass has passed through the second stage of aeration tanks the sedimentation properties of the mass becomes better and the density of suspended matter in treated wastewater reduces to 100 mg/l as a result of settling.

It is of certain interest to establish the weight of live cells of microorganisms in the sludge by the DNA content. The research into this problem has shown that the live cell weight in the first stage makes up 30% calculated on the basis of the total weight of microbial mass, and 18% in the second stage.

The third trend in stepping up the treatment is prompted by the high-rated biochemical treatment. When increasing the density of organic matter up to 8.0-15.0 g/l and the treatment rate up to 100-300 g/m^3/hour there takes place the biothermal warming-up of the liquid caused by the excessive energy emitted when the organic matter is oxidized. For instance, in the operating aeration tanks (located inside the building) the liquid temperature was maintained spontaneously at 30-34°C while the influent and the inside air had a temperature of 13-17°C. In view of this fact it is advisable to carry out treatment in the first stages under thermophilic conditions, i.e. at 50-55°C. The increase in temperature will enable to increase the treatment rate by 1.5-1.8 times if there is high-rate agitation and sufficient supply of dissolved oxygen. Thermophilic aerobic process enables to destroy practically all the pathogenic organisms in wastewater, which is a great advantage of this process. The increased demand for air which is necessary to establish aerobic conditions is the drawback of the process as it increases the cost of treatment.

The combination of the above mentioned trends enables to step up the treatment of high density waste-water and to reduce capital investments and maintenance costs.

Positive results in the field of biological water treatment intensification have been recently obtained by special preparation of waste water before delivering it into the aeration tank, the preparation is accomplished by the preliminary treatment of waste waters according to the method of electric flotation coagulation (EFC). As the result the contamination concentration is considerably reduced. F.e., the concentration of suspended matters of the butchery by electric flotation coagulation method decreased the density of suspended matters to 95-98 per cent (from 2000 to 10-60 g/m^3), COD by 60-70 per cent (from 1700-2000 to 400-800 g/m^3), BOD has been changed as well. After EFC BOD was 0.69, COD - 14.7 g/m^3.

Studies of the biological treatment of waste waters subjected to the electric flotation coagulation treatment in the aeration tanks allowed to find out a number of specific features. It was established that activated sludge differed somewhat from the sludge treating the same effluent after the usualy mechanical treatments its ash content was 15-20%, sludge index was 180-200, dehydrogenation activity of the regeneration activated sludge -5 -8 mg/g of the dry weight. Usually sludge flocs were finer and more dispersed. The composition of sludge hydrobyonts was more variable. The increase of the number of rotaria and setacious worms was observed. The process of effluent purification after RFG was rather intensive but the increase of sludge under effluent conditions was only 12.7 mg/l (2-3% of the incoming BOD), and in the contact experiments was not recorded at all. One could observe considerable increase of sludge dehydrogenation activity (up to 30-50 mg/l), sludge oxygen activity consumption, the increase of the microorganism number and the number of bacteria. The absence of notable growth of sludge may be explained by the fact that under the byological treatment of the effluent containing suspended matters the increase of sludge is connected with the sludge flocs sorption of the suspended matters constituting the inert part of the activated sludge. Suspended matters concentration in the case considered amounted to no more than 50 mg/l, i.e., was several times lower than after usual sedimentation.

High activity of sludge allowed to accomplish the purification process at reduced sludge densities. The concentrations from 0.3 to 3.9 g/l were tested. The increased doze from 0.3 to 0.8-1.0 g/l proved to be favourable for the process of contamination removal.

Changing the sludge concentration within 1.0 to 3.0 and sludge loading from 1400 to 400 mg COD/g of dry sludge respectively did not affect the duration of the process which lasted 8 hours. In all the cases the complete purification was ensured during this period of time (See Fig. 2).

The tests carried out had also to determine the setting up of sludge oxygen consumption and dehydrogenation activity. The analyses have shown that the process of impurities distraction from the liquid (sorption) and their oxydation take place with varying velocities. If the impurities removal from the effluent approximated 3 hours, the oxidation of the removed impurities required 6-10 hours. Impurities oxidation took place not only with less velocity but depended to a large degree on the sludge concentration. The higher the sludge doze was, the higher was the % of the oxidized impurities compared with those of sorbed.

The results received somewhat opposed the wide spread opinion that the necessary aeration time is the reverse ratio of sludge concentration but they are quite consistent with the laws established for natural ecological systems. Any aeration tank can be considered to be a kind of an ecological system as it has the same features: the limited capacity (biological current); the certain amount of nutrition (activated sludge); the process of energy transformation. In any ecological system the stability of existence nutrition conditions may be maintained by means of population dynamics. With the increase of the population density the growth rate is reduced. Unlike the natural ecological systems the population density in the aeration tank is artificially increased by the recirculation of activated sludge. The increased doze of sludge is necessary as it sets up the process and ensures the stability of water works operation but under these circumstances the rate growth of populations is decreased and thus their psysiological activity. By reducing ferment activity aeration tank activated sludge compensates to some extent artificially increased population density, i.e., in this way, the self-regulation of the aeration tank ecological system is achieved. Within the required sludge density its activity is determined depending upon the conditions of the ecological system as a whole.

One of the main abiotic factors influencing the formation of the ecological systems is the provision of feed. Under natural conditions the number of populations is the function of food amount. Any aeration tank does not differ in this respect from a natural ecological system. The increase of contamination concentration in the liquid treated results in the increased number of populations and the increased nutrition.

Hence the increased sludge dose is natural and efficient only in the case of highly concentrated effluent.

Increasing the sludge dose above the natural possibilities of the system causes the relative increase of the inert (ballast) part of sludge and does not set up the purification process.

The lower the sludge doze is, the more effective works every particle of the biomass, and so the same effect of purification can be achieved under different sludge density in the aeration tank.

The limits of sludge dozes when its self-regulating qualities appear under other equal conditions are determined by feeding i.e., contamination concentration in the water treated. Therefore the process of waste waters treatment is determined not only by the sludge loading but by impurities density in the aeration tank.

As sludge ensure the necessary efficiency of treatment it is more advantageous to carry out the process at the minimum sludge doze as in this case the conditions of oxygen sludge supple are improved, and thus energy consumption per unit of the contamination removed is reduced.

The EFC application as a means of preliminary effluent treatment of the butchery allows considerably to reduce the time of aeration with the subsequent treatment of this kind of effluent. Simultaniously the amoung of excess activated sludge is decreased.

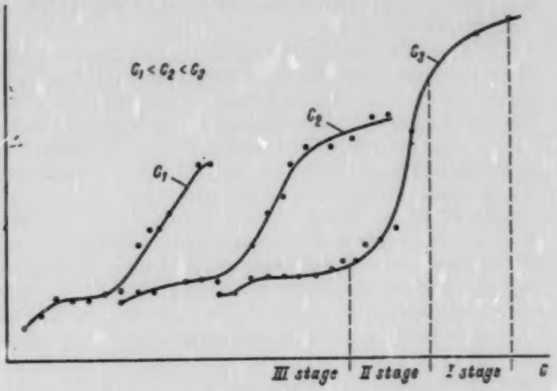


Figure 1. Oxidation impurities curves related in time.

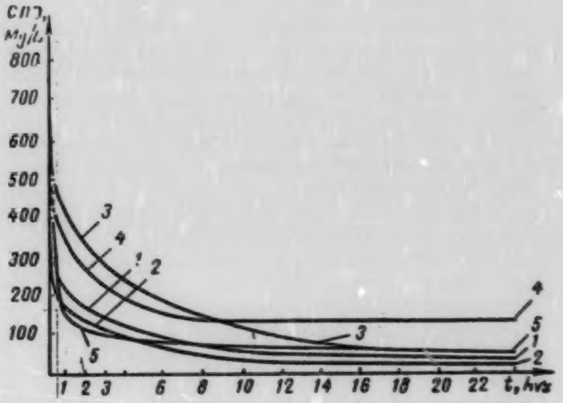


Figure 2. Kinetics of impurities distraction at various sludge doses.

	Sludge dose, g/l	Loading at the moment of stirring mg COD/g of dry sludge
1	0.40	1420
2	0.77	643
3	1.99	643
4	1.30	400
5	2.06	712

Steel Industry Wastewater Treatment Using Biological-Chemical Technology*

William J. Lacy, P.E.**

Introduction

The steel industry in the US is composed about 102 companies operating 420 plants. Of these, 63 are integrated plants, 96 are nonintegrated, and 261 are hot and cold working plants. These plants are located in almost every state, but the principal concentration is in the northeast quadrant of the country in the States of New York, Pennsylvania, Ohio, Indiana, and Illinois, see Fig. 1.

Generalizations about steelmaking operations are difficult because exceptions can be found in every mill. Steel mills in operation today range from older marginal mills built early in this century to new modern facilities built in the last several years.

Significant waterborn wastewaters result from all steel mill manufacturing operations. These wastes are principally suspended solids, oils, waste acids, ammonia, cyanides, phenols, chlorides, fluorides, sulfides, heavy metals, and heated discharges.

Basic processing operations shown in Figure 2, include: by-product coke manufacturing; sintering operations; blast furnaces; steel making (electric furnaces, basic oxygen furnaces, and open hearth furnaces); vacuum degassing operations; continuous casting; rolling mill operations; and finishing operations.

Source of Pollution

Each of these basic operations contains a large complexity of pollutant discharge into the environment. For the coking operation, wastes are emitted from the waste ammonia liquor, still wastes, final cooler wastes, and light oil recovery wastes. The blast furnace, with similar pollutants to the coking operation, has its main aqueous waste resulting from gas cleaning with wet washers. The actual steel making operation also generates liquid wastes from the air pollution control equipment, such as: sparking boxes, spray chambers, and venturi scrubbers. The degassing operation has liquid wastes from the barometric condenser cooling water. Cooling water discharge results from the casting operations, whereas, dust control equipment creates the sintering operations wastewater. The rolling mill operation has wastewater from the scale, lubricating oils, spend pickling operations, and pickling rinse waters.

Treatment technology differs for each of the respective unit operations. The coking operation employs, for the waste ammonia liquor, anhydrous recovery, bio-oxidation of cyanides and phenols, and ammonia denitrification, and possibly total incineration. Closed loop is achievable for the final cooler water with a minimum blowdown. Recycle is available for the light oil recovery wastes. The vacuum degassing operation treats its cooler water wastes by sedimentation, filtration cooling and recycle. The continuous casting mode recycles spray cooling waters with scale pit sedimentation followed by filtration or cooling. The sintering phase employs dry dust collection and gas cleaning equipment for new plants whereas the wet systems incorporate a complete recycle consisting of a thickener (polyelectrolyte addition), vacuum filter and clarifier. The recycle blowdown consists of, aeration for oil removal, lime precipitation, fluoride neutralization, and final thickeners.

The rolling mill operation (Fig. 3) employe crude settling chambers for scale and oil recovery, lime neutralization and evaporation-condensation for strong pickling wastes, recovery of oily wastewaters by primary belt skimming, chemical coagulation, magnetic agglomeration, and deep filtration. The main treatment operations employed in the finishing operations include chrome reduction, cyanide oxidation, sedimentation, and metal sludge filtration (Fig. 4).

Treatment Technology

The cyanides oxidation to cyanates (CNO-) or carbon dioxides (CO^2) by various oxidizers (alkaline chlorination or hypochlorite) has been accomplished for this industrial liquid wastes. Bioxidation is effective but generally susceptible to shock loads and requires a long residence time. Cyanide removal by ion exchange columns is effective but expensive.

The phenolic wastes can also be removed by either *liquid extraction* or *vapor recirculation* but these methods are not very economical. The *bio-oxidation* of phenols is being widely used and is economical.

Effective methods of ammonia recovery and removal require the use of an ammonia still and gas liquid adsorption. Biological nitrification-denitrification of ammonia is not feasible currently because of inherent system instabilities. However, I will discuss this process later in the paper. The ion exchange removal approach looks promising but little has been done.

Disposal of Spent Pickling Solutions

The simplest method is *neutralization* but this unfortunately leaves a great deal of dissolved solids. *Ion* exchange removal has been demonstrated for sulfuric (H_2SO_4) and hydrochloric acid (HCL). *Direct crystallization* of $FeSO_4$ from either sulfuric or $FeCL_2$ from hydrochloric liquors is possible. The acid is regenerated in the process and the entire procedure looks promising. Finally, spent pickling solution separation by reverse osmosis is now only a matter of speculation.

Industry Description

Approximately ninety-two percent (92%) of the 1972 total United States annual steel production was produced by fifteen major steel corporations. (See fig 5)

Molten iron for subsequent steelmaking operations is normally produced in a blast furnace. The blast furnace process consists essentially of charging iron ore, limestone, and coke into the top of the furnace and blowing heated air into the bottom. Combustion of the coke provides the heat necessary to obtain the temperature at which the metallurgical reducing reactions take place. The function of the limestone is to form a slag, fluid at the furnace temperature, which combines with unwanted impurities in the ore.

---

*Presented at the Joint US-USSR Water Pollution Control Symposium in Moscow, USSR, August 22-28, 1976.

***Principal Engineering Science Adviser, Office of Research and Development, U.S. Environmental Protection Agency, Washington, D.C.*

The blast furnace auxiliaries consist of the stoves in which the blast is preheated, the dry dust catchers in which the bulk of the flue dust is recovered, primary wet cleaners in which most of the remaining flue dust is removed by washing with water, and secondary cleaners such as electrostatic precipitators.

The principal steelmaking methods in use today are the Basic Oxygen Furnace (BOF or BOP), the Open Hearth Furnace, and the Electric Arc Furnace.

The steelmaking process consists essentially of oxidizing constituents, particularly carbon, down to specified low levels (less than 1%) and then adding various elements to required amounts as determined by the grade of steel to be produced (Fig. 6 shows hot slab and Fig. 7 continuous hot forming of steel tubing).

The open hearth furnace allows the operator, in effect to "cook" the steel to required specifications.

Since the introduction in the United States of the more productive basic oxygen process, open hearth production has declined from a peak of 93 million kkg in 1956 to 32 million kkg in 1971. The basic oxygen furnace is now clearly the major steelmaking process.

The electric-arc furnace (see Fig. 8) is uniquely adapted to the production of high-quality steels. Practically all stainless steel is produced in electric-arc furnaces. Electric furnaces range up to 9 meters in diameter and produce from 1.8 to 365 kkg per cycle in 1.5 to 5 hours.

Although electric-arc furnaces have been small in heat capacity as compared to open hearth or basic oxygen furnaces, a trend towards larger furnaces has recently developed. Electric-arc furnaces are the principal steelmaking process utilized by the so-called mini steel plants which have been built since World War II.

Now, I would like to discuss two biological-chemical treatments that can be applicable to steel manufacturing wastewaters; namely: A) ammonia stripping and, B) denitrification.

A. Ammonia Stripping

In the air stripping process for ammonia removal, four considerations are most significant: 1) pH of the wastewater, 2) rate of gas transfer, 3) the air-to-liquid requirements, and 4) the hydraulic loading.

In a wastestream, ammonium ions exist in equilibrium with ammonia:

$$NH_4^+ + OH \quad NH_3 + H_2O$$

Below a neutral pH of 7, only ammonium ions (NH_4) in true solution are present while, at values greater than 12, ammonia (NH_3) exists in solution as a dissolved gas. In the range of pH 7 to 12, ammonium ions and ammonia gas exist together in equilibrium. As the pH of the wastewater is increased above 7, the equilibrium shown in the equation above is shifted to the right in favor of ammonia gas which can be removed from the liquid by agitating the wastewater with air additions. The relative percentages of ammonium ions and ammonia as a function of pH and temperature are presented in Fig. 9. Examination of this Figure illustrates why very little ammonia stripping can be expected in a biological system. Even at the optimum temperature and maximum percentage of ammonia in the form of strippable gas (NH_3) is only about 25 percent.

After the ammonium ion has been converted to ammonia gas, there are two major factors which affect the rate of transfer. They are: 1) surface tension of air-water interface and, 2) the difference between the ammonia concentration in the water and in the surrounding air. It has been found that the surface tension is at a minimal value during the process of forming water droplets, and after the water droplet has been formed, gas transfer becomes negligible. Therefore, repeated droplet formation, rupture, and reformation greatly assist ammonia stripping operations with regard to minimizing surface tension.

Minimizing the concentration of ammonia may be accomplished by circulating large quantities of air rapidly through the water droplets. These same principles of droplet formation and reformation and the necessity of large gas/liquid requirements are inherent in conventional cooling tower design and explain the adaptability of these towers to the ammonia stripping process. The material value can be described as

$$G(Y_1 - Y_2) = L_Q(x_1 - x_2)$$

Where:
G = Quantity of air flow, moles incoming air/unit time
L_Q = Quantity of water flow, moles incoming water/unit time
Y_1 = Concentration of ammonia in air at the bottom of the tower, moles ammonia/mole air
Y_2 + Concentration of ammonia in air at top of tower, moles ammonia/mole air
X_1 = Concentration of ammonia in water at the bottom of the tower, moles ammonia/mole water
X_2 = Concentration of ammonia in water at top of tower, moles ammonia/mole water

This equation is based on a mass balance of input and output and is valid regardless of the internal conditions which control the process. Fortunately, the internal equilibria are governed by Henry's Law for which adequate knowledge exists and which will not be described. The molar ratio of ammonia in the gas and liquid remain constant at a specified temperature and pressure.

Design and Operational Considerations

Very few ammonia stripping towers have been designed for treatment of wastewaters; generally, those towers which have been constructed were the for treatment of low strength municipal wastewaters. The same principles utilized in the design of conventional cooling towers are also applied to the design of ammonia-stripping towers. The crosscurrent design is the more prevalent. Although the counter-current type may become popular as more field data become available.

There is greater efficiency of ammonia removal with increased depth of tower packing. It should be noted that the minimum air/liquid loading required to obtain 90 percent removal is approximately 2,000 liters of air per liter of wastewater. The increased removals at greater depths are probably due to the greater number of droplet formations and the subsequent air-water contact afforded by the greater depth of packing.

Deeper tower packing shows little effect of hydraulic flow rate, at less than 100 L min/m^2, at hydraulic loadings greater than 100, sheeting of the water is observed which decreases the number of droplet formations and subsequently reduces the tower efficiency.

Aside from economic considerations, the major advantage of ammonia stripping over other methods of ammonia removal is the ability to control the level of ammonia removed in the process. Disadvantages are also inherent to the air stripping process as outlined below:

1. Cold weather operation
    a. Ammonia solubility greatly increases with lower temperature
    b. Inability to operate tower at wet bulb temperatures less than 0°C
    c. Fogging and icing problems
2. Deposition of calcium deposits within tower from pH adjustment with lime.
3. Air pollution problems.
4. Ammonia reaction with sulfur dioxide to form aerosols.
5. Deterioration of wood packing due to high pH of wastewaters.

In the case of industrial wastes where the ammonia concentration of the wastewater may be extremely high, on the order of several thousand mg/l, an air pollution problem may develop. Other potentially troublesome problems may develop near large metropolitan areas or other regions in which high concentrations of sulfur dioxide form an aerosol or fog. In light of the above disadvantages, ammonia stripping is a practical, reliable method for nitrogen removal under the right climatic conditions and with the proper precautions regarding scale prevention or removal.

B. Nitrification-Denitrification

In the destruction and assimilation of organic compounds, biological organisms will require, as nutrients, approximately 1 kg of nitrogen per 23 kg of BOD removed. In estimating nitrogen removal through a system by synthesis, only the BOD removed and not that applied should be considered. The nitrogen which is removed by synthesis is incorporated, at least temporarily, into the microbial cell, and is eliminated by removal of excess sludge from the system. A system with poor settleability properties cannot be expected to demonstrate a total removal of 1 kg of nitrigen per 23 kg BOD due to the high carry-over of organisms in the effluent. In this case, mixed media filtration may be required to achieve the desired effluent quality. Also, if the system has an excessive detention time or over 6-8 days sludge age, nitrogen in the form of ammonia or organic nitrogen may be released back into solution so that once again an assumed removal of 1 kgN/23 kg BOD removed would not be valid.

During the process of biological nitrification, ammonia and some organic nitrogen forms are converted to nitrite and nitrate compounds by a specific set of organisms, *Nitrosomonas* and *Nitrobacter*. These organisms are strictly aerobic autotrophs, i.e., they obtain carbon from inorganic sources such as CO_2, HCO_3, etc., and do not employ the same metabolic mechanisms as those organisms which assimilate BOD materials. The nitrifiers reproduce and grow at much lower rates than the BOD removing organisms and thus compete in the same environment. For example, in an activated sludge system a constant concentration of organisms or suspended solids (MLVSS) is desired, so that all excess sludge which is produced and accumulates is periodically wasted. If the BOD removing organisms are producing at a rapid rate, they will increase the required wastage of sludge from the system, which will generally be much higher than the wasting rate compatible with maintenance of an adequate population of nitrifiers. Thus, insufficient nitrification will result unless the wastage rate is lowered to accommodate the nitrifier requirements. The wastage rate is usually controlled to maintain a sufficient, "sludge age" in the system for nitrification.

It is claimed that a sludge age greater than 4 days in the activated sludge process is adequate for 90 percent nitrification at 20°C. I caution you that this information was developed for municipal wastes and should never be applied to higher strength industrial discharges without extensive pilot studies.

Biological nitrification of ammonia concentrations as high as 500 mg/l with greater than 90 percent removal can be obtained with the single-stage activated sludge process. Two-stage systems have achieved greater than 97 percent removal with these high influent levels. The biological process can be applied to high as well as low concentrations of ammonia assuming proper conditions of pH, temperature, absence of inhibitors, etc.

The nitrifiers are biological organisms, and are subjected to the same constraints which limit most biological systems, i.e., temperature, toxicity, shock loading, pH, etc. Nitrification has generally been found most efficient in the pH range of 7.8 to 8.3, and pilot results have indicated that inefficient nitrification systems can be improved by adjusting the influent pH level so that the aeration basin contents are within the optimum range. Sodium hydroxide is recommended for the pH adjustment since lime may precipitate calcium carbonate and limit the system from the standpoint of available inorganic carbon, particularly with high ammonia wastes. Lime may be satisfactory for low-strength ammonia wastewaters.

Compounds toxic to nitrifiers include heavy metals, cyanides, halogenated compounds, phenols, mercaptans, and thiourea. Trace amounts of these constituents may not nullify nitrification, but could lower the rate coefficient, k_n. Pilot studies would then be required prior to design or "washout" because retarded growth rate may occur in the final system.

Optimum temperature for nitrification has been cited as 28-32°C with nitrification ceasing below 5°C. If severe temperatures are anticipated (less than 12-15°C in the aeration basin), then serious consideration should be given to the feasibility of nitrification. It is possible to preheat the influent wastestreams, but this is not a practical solution with most large streams.

Nitrate and nitrated compounds are very difficult to treat by physical and chemical techniques other than ion exchange. However, ion exchange technology for nitrogen compounds is applicable to a small percentage of wastewaters. Consequently, biological mechanisms remain the most practical and dependable methods for removing nitrate constituents from wastewaters. Biological nitrate reduction can be accomplished by assimilatory or dissimilatory mechanisms. Assimilatory reduction occurs when nitrate-nitrogen is utilized as a source of nitrogen for synthesis by initial conversion to ammonia and subsequent incorporation into the cell. Nitrate dissimilation involves biological oxidation of organic compounds where nitrate serves as the terminal hydrogen acceptor in place of molecular oxygen. The end product of this reaction may be nitrite, ammonia, nitrous oxide or nitrogen gas depending on the organisms and the pH of the system. Practically, the anaerobic denitrification process will oxidize degradable organic carbon compounds and reduce nitrate to harmless nitrogen gas.

The denitrification process has been effectively applied to nitrate levels as high as 10,000 mg/1. Currently, three denitrification systems, anaerobic activated sludge, anaerobic ponds, and upflow anaerobic filters offer good reliability with variable economy. If the nitrate treatment occurs after BOD removal, there may be insufficient carbon present for reduction of the nitrate and an external source will be required. Methanol has been most commonly cited as the most economical external carbon source based on cost and available carbon. Carbon addition, whether methanol or a suitable industrial waste, is required for all denitrifying systems which follow organic removal processes. In many instances, particularly in those with high strength industrial wastes, the economy of the system will depend on the external carbon source chosen.

With many industrial processes, e.g., where nitric acid is employed in-plant, it is much more desirable to pretreat the waste for nitrate reduction ahead of a BOD removal system, such as activated sludge. In this manner, readily-available carbonaceous BOD in the raw waste is utilized for the denitrifying carbon source. This concept not only reduces the costs for external carbon in a post-treatment scheme, but will also reduce the subsequent aeration volume and horsepower needed for the activated sludge system due to the BOD reduction through the denitrification system.

Besides ammonium stripping and denitrification, some other technologies to be implemented in the near future include: slag and sludge dewatering and disposal, technology development for a closed loop in an interested steel mill reducing phosphates and heavy metals, employment of electro-membranes in the H_2SO_4 pickling operation to achieve a step towards closed cycle, and finally a new technology is emerging using direct reduction of low grade taconite ore effectively eliminating the blast furnace and coking operation to achieve total environmental control.

All of these aforementioned technologies will be attempted in the near future by the Environmental Protection Agency to improve the steelmaking industries' technology and to preserve the integrity of the United States waterways.

References

1. Lacy, W.J., G. Rey and H.G. Keeler, *Projects of the Industrial Pollution Control Division,* U.S. Environmental Protection Agency, Office of Research and Development, Washington, D.C. 1974.
2. Cywin, A., E. Dulaney, *Development Document for Effluent Limitation Guidelines for the Steel Making Segment of the Iron and Steel Manufacturing Point Source Category,* USEPA, Office of Water and Hazardous Materials, Washington, D.C., June 1974.
3. Adams, C.E., W.W. Eckenfelder, *Process Design Techniques for Industrial Waste Treatment,"* Enviro Press, Nashville, Tennessee, 1974.
4. Lacy, W.J. *Point Source Control—EPA Industry R&D Cooperation, Chemical Technology,* Vol. 5, pp. 742-747, December 1975.
5. *Pollution Abatement Costs and Expenditures 1973.,* U.S. Department of Commerce, MA 200(73)-2, Issued 3/19/76

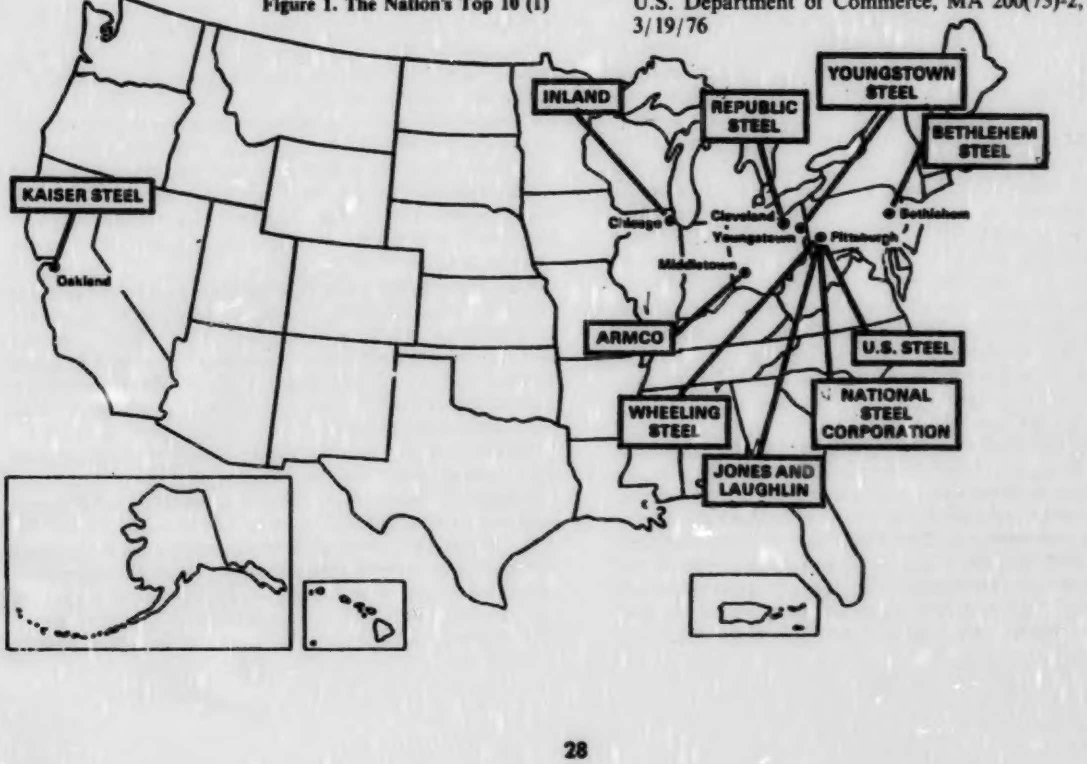


Figure 1. The Nation's Top 10 (1)

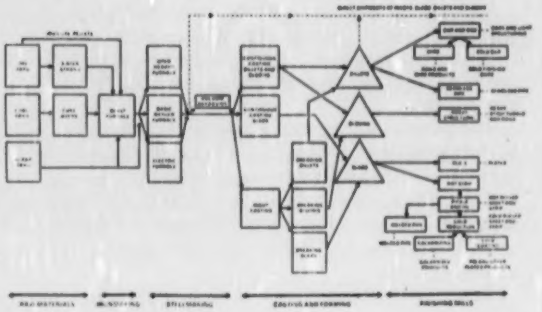


Figure 2. Steel Production Processes (2)

Table 1 *United States Annual Steel Production Major Producers (2) 1972*

	Metric Tons/Year
United States Steel	31,750,000
Bethlehem Steel	19,960,000
Republic Steel	9,980,000
National Steel	9,520,000
Armco Steel	7,710,000
Jones and Laughlin Steel	7,280,000
Inland Steel	6,800,000
Youngstown Sheet and Tube	5,440,000
Wheeling Pittsburgh	3,540,000
Kaiser	2,720,000
McLouth	1,819,000
Colorado Fuel and Iron	1,360,000
Sharon	1,360,000
Interlake	907,000
Alan Wood	907,000

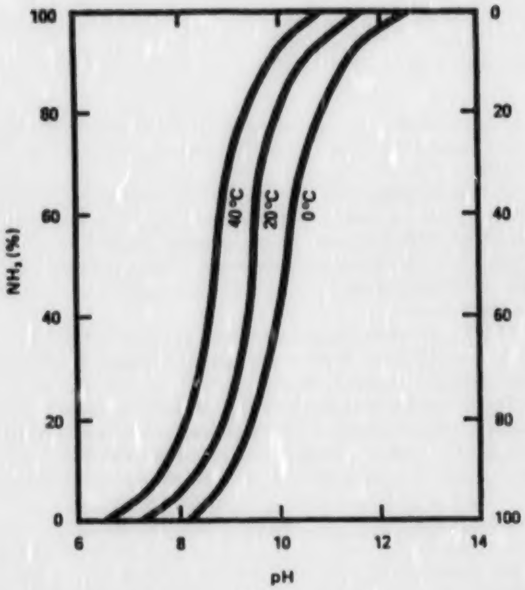


Figure 3. Distribution of Ammonia and Ammonium Ion with pH and Temperature (3)

8 BIRLEC 50 Ton Electric Arc Furnace at Manchester Steel

Inland Steel Company's highly automated slabbing mill can handle ingots weighing as much as 55,000 pounds . . . either singly or two in tandem. It can roll the top, bottom, and both edges simultaneously resulting in better, more uniform grain structure and increased yield.

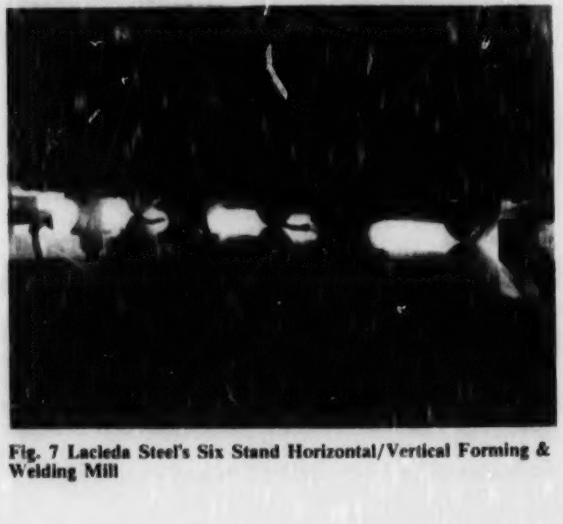


Fig. 7 Lacleda Steel's Six Stand Horizontal/Vertical Forming & Welding Mill

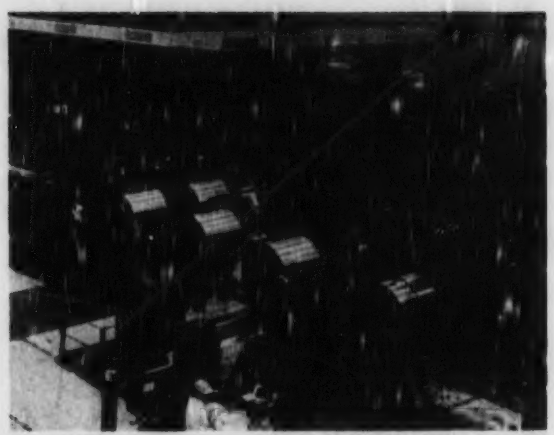


Fig. 3 Inland Steel's 80 inch Five Stand Cold Rolling Mill and Pickle Line.

Facilities Improvement for Biochemical Treatment of Petroleum Refinery Wastewater.

V.Ya. Gerber

Bashkirian Scientific Research Institute of Petroleum Refining (USSR)

Summary

This paper presents estimated performance specifications for designing biochemical treatment facilities at refineries and petrochemical plants.

The choice of single- and two-stage treatment systems for refinery and petrochemical sewage is recommended depending on the quality of the sewage.

There are provided some operational data for refinery and petrochemical sewage treatment and advanced treatment as well as the flow diagrams and structures of activated sludge units used. The advantages of activated sludge units over biological filters and those of two-stage systems over single-stage systems are demonstrated.

The quality of biological sewage treatment effluent and the ratio of dilution for it to be harmless for receiving water is reported.

In the Soviet Union biochemical treatment is one of the basic treatment processes preceding the refinery waste discharge into receiving waters.

The biochemical treatment has widely been used for treating refinery wastes. Treatment facilities of all the petroleum refineries and petrochemical plants situated in the Volga and Urals basins include biochemical treatment plants. The latter plants are foreseen for all the petroleum refineries and petrochemical plants under construction.

Refinery wastewater can be subjected to biochemical treatment either alone or diluted with domestic and chemical wastewaters. In the first case biogenous elements, especially nitrogen and phosphorus, are to be added to the wastewater.

The biochemical treatment equipment of Soviet refineries is mainly presented by activated sludge systems, especially those with a many-point waste feeding and a complete mixing. Most commonly conventional activated sludge units (with a one-point waste and activated sludge feeding to the first channel of the unit) are used at the second treatment step.

As a matter of fact, no use is made of biological filters for oil-containing waste treatment at the Soviet refineries, as the operating experience at a refinery has shown them to be insufficiently efficient, BOD$_5$, oil, and phenols removals being as low as 73, 29, and 72%, respectively. The use of activated sludge units at the same refinery has improved the BOD, oil, and phenols removals up to 93 to 95%, 80 to 84% 99 to 100%, respectively.

Oxidation ponds at domestic refineries only serve for after-treatment of a biochemical treatment effluent.

As the laboratory investigations and the operation experience have shown, the treatment efficiency of two-step facilities is by 10 to 15% better in comparison to that of single-step facilities, in terms of both BOD and oil removals. The operation of two-step facilities creates conditions stimulating adaptation of the second-step activated sludge microorganisms for uptake of difficult-to-oxidize substances. Therefore, most petroleum refineries use a two-step biochemical treatment. The treatment efficiency of these facilities for oil-containing wastewater is as follows:

BOD removal	93 to 98%
oil removal	77 to 86%
phenols removal	99 to 100%

The same result can be achieved in single-step activated sludge units by increasing the total aeration duration by 30 to 35%.

Special investigations have shown that only about 20% of ether-soluble substances contained in a biochemical treatment effluent are hydrocarbons originated from petroleum, the remaining substances being decomposition and oxidation products which do not undergo complete biodegradation.

Thus, petroleum hydrocarbons account for 2 to 3 mg/l out of 8 to 12 mg/l of ether-soluble substances in a refinery biochemical treatment effluent.

The operation data has shown that when using two-step biochemical treatment of refinery wastewater in activated sludge units and an advanced treatment in oxidation ponds the following composition of the final effluent is obtained:

COD, mg O^2/l	60 to 80
BOD^5, mg O^2/l	2 to 8
Ether-solubles	4 to 8
Oil	1 to 2
Phenols	0.0 to 0.002

Thus, the use of a complete biochemical treatment of refinery wastewater followed by its advanced treatment makes it possible to minimize the amounts of pollutants to be discharged to receiving waters. However, a long-term wastewater treatment in activated sludge units, big volumes of facilities and a high electric energy consumption stimulate the search of intensification ways for lessening this process capital and operation costs. Therefore, investigations are carried out in the USSR to intensify the biochemical wastewater treatment process in activated sludge units, to reduce their aeration duration, and to diminish the facilities sizes and treatment costs.

The intensification of biochemical treatment of oil-containing wastes is possible by raising the activated sludge and dissolved oxygen concentrations as well as by the facilities hydrodynamics improvement.

For a process with high sludge doses most suitable are integrated facilities (aero-accelerator type) which are equipped with pneumatic mechanic aeration systems and are combined with a settler. The combined construction of facilities makes it possible to achieve maximum treatment efficiency with low space requirements. The oxygen quantity fed into the facility can be changed by changing automatically the aerator rotation rate. The use of flotators instead of secondary settlers makes it possible to increase the sludge dose in an activated sludge unit. Thus, at a petroleum refinery a two-step plant for biochemical treatment has been tested, with a flotator provided for the first step sludge separation. Due to the flotator it is possible to maintain a higher activated sludge dose in the activated sludge unit. However, during aeration using air the intensified biochemical oxidation at high activated sludge doses can give rise to anaerobic conditions in the activated sludge unit, which adversely affects the treatment process.

The aeration using technical oxygen instead of air is a promising method to intensify the process of wastewater biochemical treatment. The performed investigations have shown the replacing of air with technical oxygen to be capable of shortening the aeration duration when treating oil-containing wastewater by a factor of 4 to 6 and to lessen accordingly the volume of activated sludge units in comparison to conventional air aeration or to increase their capacity. The replacing of air with technical oxygen dramatically raises the dissolved oxygen concentration in a facility. Good oxygen regime in an activated sludge unit makes it possible to increase the activated sludge dose.

Changing from air to oxygen for aeration results in considerably better properties of the activated sludge: little or no thread bacteria, no swelling, and improved settleability. Therefore, suspended solids in a secondary clarifier effluent do not increase in spite of increasing sludge concentration. Also, the use of technical oxygen contributes to nitrogen and phosphorus removals.

The substitution of technical oxygen for air requires special design reactors: tight, with mechanical mixing of sludge liquor and oxygen reuse.

Two types of facilities destined to using technical oxygen have been developed in the USSR: countercurrent aerotank - a clarifier with airlift circulation and oxytank - a tight aerotank with mechanical aeration, combined with sludge separator. In the oxytank the efficiency of oxygen utilization achieves 95%. New design biooxydizers are adapted for operating with high sludge doses of 10 to 15 g/1, which, along with increasing oxygen concentration up to 8 to 10 mg/1, raises the oxytank oxydation capacity up to 5 to 10 kg BOD^{total}/m^3 day. The oxytank was tested for chemical plant wastewater under semicommercial conditions.

Technical and economical calculations have verified the profitability of using oxygen for wastewater biochemical treatment. The use of oxytanks for industrial wastewater treatment is most profitable when oxygen is supplied by air fractionation departments of industrial plants.

The wastewater biochemical treatment equipment is persistently improved to enable an advantageous use of oxygen even in those cases when it is to be produced specially for wastewater treatment.

In recent years, much emphasis has been placed on the hydrodynamics improvement of aeration facilities.

In the Soviet Union and abroad various types of activated sludge units are widely used. Their basic types include completely mixed and plug flow systems as well as intermediate types.

According to the theory of chemical reactors and the theoretical analysis of kinetic models used now for organics biochemical oxidation in activated sludge units, the oxidation degree of starting materials in a completely mixed activated sludge systems (for a zero order reaction) is above that in a plug flow activated sludge system at equal facility volumes. However, the practice of treating wastewater has shown the completely mixed activated sludge system to be superior to other systems in many respects, for the most part in that it contributes to a fail-free performance at an immediate concentrated wastewater influent. Therefore, the completely-mixed activated sludge system as well as that with a many point wastewater feed (intermediate type) have found wide application for petroleum refining wastewater treatment.

Large-scale flow studies in various types of activated sludge systems have shown the flow conditions of even long conventional plug flow activated sludge systems to approach those of complete mixing. Thus, various types of large-scale activated sludge systems achieve essentially the same efficiency.

Laboratory and pilot data have shown a specially designed activated sludge system to perform more efficiently than a conventional one, which allows a 1.5 to 2-fold reduction in the facility volume.

Thus, the use of combined facilities with high sludge doses, specially designed activated sludge systems, and technical oxygen instead of air makes it possible to considerably intensify the biochemical treatment process for petroleum refining wastewater and to reduce capital and operating costs.

Quality requirements for waste discharge into receiving waters are now stringent both in the Soviet Union and abroad. This makes it reasonable to subject biochemically treated petroleum refinery wastewater to an advanced (tertiary) treatment such as filtration, treatment improvement, the use of such methods for a biochemical treatment effluent leads to diminishing sizes of biochemical treatment facilities.

Biological Methods for Control of Nitrogen in Municipal Wastewaters

William A. Rosenkranz*

**Director, Waste Management Division*
Office of Research and Development
Environmental Protection Agency
Washington, D.C. 20460USA

Various compounds containing the element nitrogen are becoming increasingly important in wastewater management due to the many effects that nitrogenous materials in wastewater can have on the environment. Nitrogen, in various forms, can deplete dissolved oxygen levels in receiving waters, stimulate aquatic growth, exhibit toxicity toward aquatic life, affect disinfection efficiency, present a public health hazard and affect the suitability of wastewater for reuse.

Biological and chemical processes which occur in wastewater treatment plants and in the natural environment can change the chemical form in which nitrogen exists. Such changes may eliminate a deleterious effect of nitrogen, while producing, or leaving unchanged, another effect. For example, by converting ammonia in raw wastewater to nitrate, the oxygen-depleting and toxic effects of ammonia are eliminated, but the biostimulatory effects may not be changed significantly.

Most of the nitrogen in raw municipal wastewater is usually in the ammonia form, although 30 percent to 50 percent is normally associated with organic matter. Nitrogen is removed in various ways in wastewater treatment facilitiles. A large portion of the organic nitrogen is removed by primary sedimentation, while additional amounts of organic nitrogen may be biologically converted to ammonia when the wastewater is subjected to secondary treatment such as activated sludge. Nitrates and nitrites usually absent in raw wastewater, may be present following a highly efficient secondary treatment process and the presence of signigicant numbers of nitrifying bacteria.

Effective methods of wastewater treatment which will remove nitrogen are increasingly needed in many locations where critical water quality conditions exist. Governmental agencies have promulgated effluent standards relating to water quality in an attempt to relieve or prevent the symptoms of nitrogen pollution in such locations. Scientists and engineers have devoted considerable research and development effort toward developing both biological and physical-chemical methods for nitrogen removal in order to produce effluents which can be discharged into streams which require such action for achieving acceptable water quality.

Physical-chemical methods which have been shown to be effective depending on effluent quality requirements include:

1. *Breakpoint Chlorination*—Addition of chlorine to wastewaters for the purpose of oxidizing the ammonium ion to end products composed predominately of nitrogen gas.
2. *Selective Ion Exchange for Ammonia Removal*—Use of an ion-exchange resin which is selective for ammonium. A natural zeolite, clinoptilolite, occurring in the Western United States has been found effective for this purpose.
3. *Air Stripping of Ammonia*—Countercurrent circulation of large volumes of air and effluent through a stripping tower after the treated effluent has been adjusted to high pH.

Biological methods of removing nitrogen, the subject of this paper, consist of two wastewater treatment phases: nitrification and denitrification. The processes which have been used for this purpose utilize several configurations, but all involve first the nitrification step, followed by a denitrifaction step. Certain controlling factors form the basis of configuration selection. Nitrification by autotropic bacteria (Nitrosomes and Nitrobacter) achieves a maximum rate in the activated sludge process at dissolved oxygen concentration of about 2 mg/l or above. The rate decreases to zero as the dissolved oxygen concentration decreases to zero. While denitrification by facultative bacteria occurs in both anoxic and slightly aerobic systems, the most rapid denitrification occurs with dissolved oxygen concentration of zero. Ample sources of readily acceptable organic carbon to serve as an energy supply for the bacterial reduction of the nitrate and nitrite are required.

In biological treatment of wastewaters, oxidation of carbonaceous material, nitrification, and denitrification all occur within a single process if sufficient bacterial solids retention time is provided for development of the nitrifying and denitrifying organisms. Optimum process operating conditions for oxidation and for subsequent denitrification are thermodynamically antagonistic. The presence of the more powerful oxidant oxygen (electric acceptor) suppresses the use of NO_3 (electron acceptor) in the biological oxidation of the carbonaceous material in the wastewater. In conventionally aerated biological systems, efficient oxidation of the carbonaceous and nitrogenous materials, in either a single or two-stage process, is achieved under aerobic reactor conditions. The aerobic conditions produce the nitrate product, but also remove the organic materials which act as readily available electron donors for denitrification. In addition, the dissolved oxygen in the water significantly suppresses or minimizes the biological reduction of the nitrate or nitrite as they are produced.

Although the biological potential exists in municipal wastewaters for both nitrification and denitrification without supplemental organic carbon sources, the operating conditions usually employed in aerobic biological processes produce efficient carbonaceous removal and nitrification but not efficient denitrification. Thus, the operating conditions for the activated sludge process must be selected which will produce efficient nitrification and denitrification with the indigenous carbonaceous material in the wastewater acting as the electron donor during denitrification.

Research to accomplish this objective was undertaken at the EPA Pilot Plant at Washington, D.C. The approach to achieving nitrification—denitrification in a single, activated sludge reactor-clarifier with the wastewater organic carbon used for denitrification consisted of providing alternate periods of aerobic and anaerobic conditions within the reactor and operating the reactor at sufficiently low food-to-microorganism ratios (high solids retention times) to ensure a nitrifying population within the mixed liquor culture. To provide the alternating aerobic-anaerobic conditions while continuously operating the air compressor, the activated sludge reactor was divided into two equal basins operating in series. Each basin, with a water depth of 3.35 m (11 ft.), provided a detention time of 3.55 hr., at a process flow of 189 cu m/day (50,000 gpd). Air was supplied alternately to each basin; first to one basin and then to the other on a 30-minute cycle. The dissolved oxygen in the basins was manually controlled at between 2 and 3 mg/l during aeration and rapidly decreased to zero during the anaerobic period.

Mechanical mixers in each basin, operated at 30 rpm, suspended the mixed liquor solids without any significant surface aeration of the wastewater. Figure I illustrates the pilot plant configuration.

Nine months of test data are shown in Table I. During 9 months of operation, the pilot plant operated at a F/M (food-to-mass ratio) of approximately 0.1 lb BOD$_5$/lb. MLVSS/day (0.1 g/g/day) expressed on the basis of the total inventory in the reactor. This F/M was sufficiently low to permit the development of a mixed culture of organisms for carbon oxidation, nitrification and denitrification. Total nitrogen removal efficiencies were highest at the higher COD/TKN ratios.

Nitrogen removals during the study varied from 54 to 84 percent. As in other alternating aerobic/anoxic studies, it was found that a severe filamentous bulking condition developed in the sludge, limiting wintertime clarifier overflow rates to about 12.24 cu m/day/sq m (300 gpd/sf). Bulking sludge had been observed during operation of this pilot study at low temperatures and at low F/M operation here and at other plants. It appeared that clarifier would limit operation of this aerobic/anoxic system as it will other similar systems.

On March 1, 1975, the Office of Research and Development funded a full-scale plant evaluation project of the above described process at Owego, New York. The plant operates over a range of wastewater temperature of 5°C to 20°C. The objective of the project was to maximize nitrogen removal by simple changes in operational techniques.

The plant is designed for 7,570 cu m/day (2 mgd) at the design date of 1990. Present flow averages 1,514 cu m/day (0.4 mgd), with a maximum dry weather flow of 2,271 cu m/day (0.6 mgd) and a minimum of 1,135 cu m/day (0.3 mgd). The plant does experience the impact of infiltration since high flows of 3,406 cu m/day (0.9 mgd) have been recorded. Facilities consist of dual primary settlers and aerators (Figure II). Each reactor has two compartments and each compartment has one surface aerator. The compartments are sized for contact stabilization; with the larger units having 15 horsepower and the smaller 10 horsepower surface aerators. Dual final clarifiers are fitted with chain drags and scum baffles. Sludge is digested in a two-stage anaerobic digester. Sludge is hauled to nearby farms and disked into the soil.

In line with our findings at the Blue Plains pilot single stage system that a rather high BOD/TKN ratio is needed for denitrification, the Owego primary clarifiers were taken off line. The aerators received raw wastewater with a BOD$_5$ of approximately 200 mg/l and a total nitrogen content of approximately 40 mg/l.

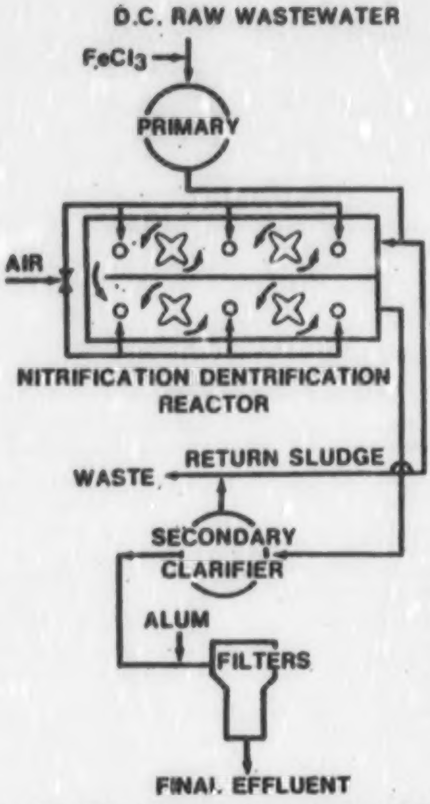


Figure 1 Blue Plains Alternating Anoxic-Aerobic System

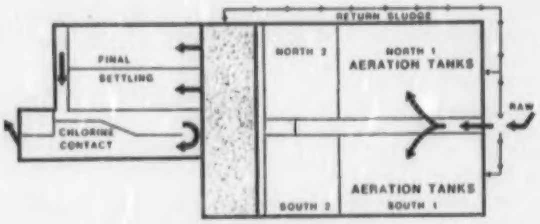


Figure 2
Extended Aeration
Water Pollution Control Plant
Town of Owego, New York

MONTH 1973	DET. TIME HR	F/M LB BOD APPLIED/LB MLVSS/DAY OR G/G/DAY	MLSS MG/I (% VOLATILE)	SVI, ML/G	COD/TKN RATIO	TEMP., C	INFLUENT QUALITY MG/I BOD5	SS	TOTAL KJELDAHL NITROGEN	EFFLUENT QUALITY MG/I[a] BOD5	SS	TOTAL KJELDAHL NITROGEN	NO3/NO2-N	REMOVALS, PERCENT BOD5	SS	TOTAL NITROGEN
JAN	12.3	0.072	3510 (74)	245	9.6	14.0	96.5	110	25.7	20.4	15.4	2.28	3.99	79	85	76
FEB	12.3	0.066	3980 (73)	250	9.9	14.2	99	108	23.2	14.0	14.3	1.52	4.41	86	87	75
MARCH	12.3	0.10	2950 (73)	330	10.5	15.5	110	128	24.8	6.5[b]	13.0	4.20	2.30	94[b]	88	74
APRIL	12.4	0.081	3540 (67)	277	10.6	–	98.8	120	21.7	5.3[b]	13.0	5.20	6.03	95[b]	89	49
MAY	10.5	0.089	4170 (69)	227	10.0	–	115	109	23.3	3.3[b]	11.8	1.36	8.25	97[b]	89	59
JUNE	8.8	0.105	4010 (69)	188	10.3	23.0	107	112	24.0	3.2[b]	7.8	1.51	2.3	97[b]	93	84
JULY	6.8	0.093	3040 (64)	133	7.9	25.0	51	153	15.0	3.8[b]	9.0	2.14	2.72	93[b]	94	68
AUGUST	6.6	0.089	3200 (57)	134	7.5	25.5	44.2	197	14.9	2.6[b]	10.0	1.23	3.74	94[b]	95	67
SEPT	8.7	0.11	3700 (65)	–	10.0	26.0	99	110	22.6	7.2[b]	16.0	10.2[c]	0.2[illegible]	93[b]	85	54

[a] PRIOR TO FILTRATION
[b] NITRIFICATION INHIBITED
[c] AMMONIA LEVEL WAS 9.4 MG/L AS N (SEE TEXT)

Table 1 Summary of operation and performance for the Blue Plains Alternating Aerobic/Anoxic System (Reference 60)

After a brief start-up period, it was determined that the plant was operating well and that conditions were suitable for pulsing the surface aerators to encourage denitrification. Again, on the basis of Blue Plains experience, a 50 percent cycle was set for the initial period of study. The aerators would be on for 30 minutes and off for 30 minutes. The project included plans to collect data during warm and cold weather. The warm weather data was collected up to September of 1975. The cold weather data collection period was scheduled to begin in January of 1976.

Performance of the Owego plant has been very good. For the period through September of 1975, BOD_5 and suspended solids removals were better than 90 percent, nitrification was complete, and total nitrogen removals were in excess of 80 percent without the addition of an organic supplement. At times total nitrogen removal approached 95 percent efficiency.

This project is nearly complete. The cold weather data is undergoing analysis. Based on the on-site experiences, the process appears to be relatively easy to operate. It has been observed that Nocardia growths have not appeared during the report period. We expect that the process could be made to operate automatically with the proper sensors to monitor the effluent for the degree of nitrification and/or denitrification required.

As mentioned earlier, there are several processes or process configurations that can be used for nitrogen removal. The Pasveer ditch, or endless channel system can be effective in removing nitrogen. Removals of 90 percent have been reported. This system is illustrated in Figure III.

EPA funded an evaluation project of this type of system at Dawson, Minnesota. The Dawson plant is designed to treat 984 cu m/day (0.26 mgd) having a strength of 230 mg/l BOD_5 and 200 mg/l suspended solids. One of the objectives of the study was to determine the feasibility of nitrifying and denitrifying the wastewater without the addition of an alternate carbon source (for denitrification).

Nitrification-denitrification efficiency is linked to the concentration of dissolved oxygen in the channel. In the zone that experiences a D.O. of greater than 0.5 to 1.0 mg/l, nitrification will occur. In the zone where D.O. is less than 0.5 mg/l, denitrification will take place without the addition of an alternate carbon source such as methanol. Instead, the raw BOD acts as the carbon source. Denitrification is limited by the ratio of BOD (or COD) to TKN. The higher the ratio the more efficient the process.

Even though the plant was not operated in the most optimum mode, removals ranged from approximately 50 to 80 percent. As stated earlier, the Dutch and others have reported removal of nitrogen in excess of 90 percent.

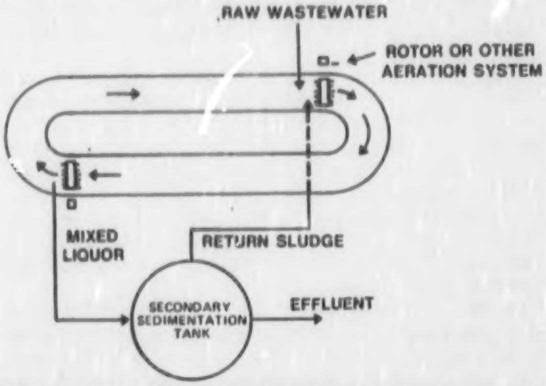
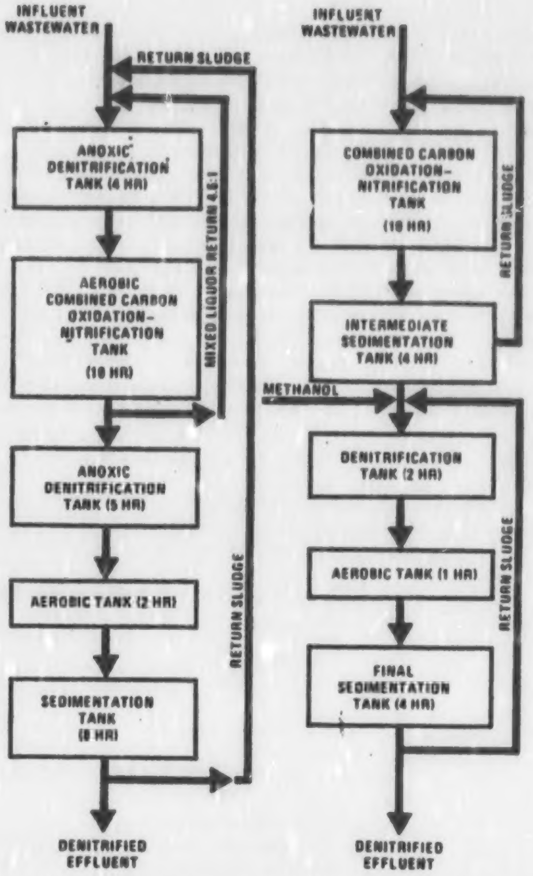


Figure 3 Pasveer ditch or Endless Channel System for nitrogen removal

Figure IV shows two additional systems, one of which utilizes methanol as a carbon source.

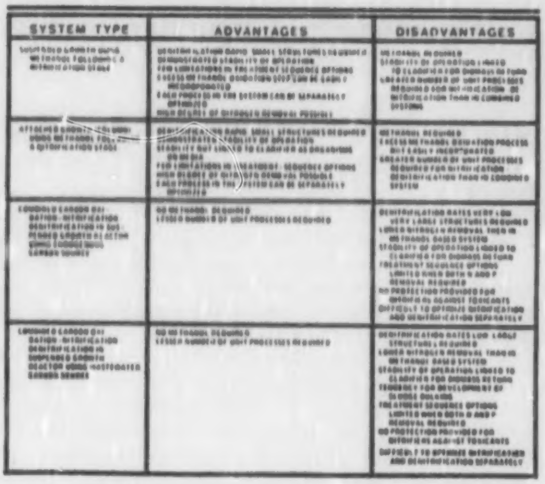
The advantages and disadvantages of the several biological nitrogen removal systems are summarized in Table II.


INFLUENT WASTEWATER
RETURN SLUDGE
ANOXIC DENITRIFICATION TANK (4 HR)
MIXED LIQUOR RETURN 4.6:1
AEROBIC COMBINED CARBON OXIDATION-NITRIFICATION TANK (18 HR)
ANOXIC DENITRIFICATION TANK (5 HR)
AEROBIC TANK (2 HR)
RETURN SLUDGE
SEDIMENTATION TANK (8 HR)
DENITRIFIED EFFLUENT
INFLUENT WASTEWATER
COMBINED CARBON OXIDATION-NITRIFICATION TANK (10 HR)
RETURN SLUDGE
INTERMEDIATE SEDIMENTATION TANK (4 HR)
METHANOL
DENITRIFICATION TANK (2 HR)
AEROBIC TANK (1 HR)
RETURN SLUDGE
FINAL SEDIMENTATION TANK (4 HR)
DENITRIFIED EFFLUENT

A. BARDENPHO PROCESS (29 HR)

B. ALTERNATIVE METHANOL BASED SYSTEM (21 HR)

Figure 4 Comparison of Denitrification Systems



SYSTEM TYPE	ADVANTAGES	DISADVANTAGES
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

Table 2. Comparison of Denitrification Alternatives

References

Bishop, D.F., et al, *Single Stage Nitrification-Denitrification,* Environmental Protection Series, EPA 670/2-75-051, June 1975

Grounds, Harry C., Draft Final Report *Dawson, Minnesota Demonstration Project,* U.S. EPA Grant No. 803067-01-1, December 1975

Personal Communication w Donald E. Schwinn (Stearns and Wheler Civil and Sanitary Engineers), May 6, 1975 in reference to Owego, New York/EPA Demonstration Project: *Full-Scale Operation of a Single-Stage Nitrification-Denitrification Plant*

Schwinn, Donald E., Quarterly Report on *Single-Stage Nitrification Denitrification Full-Scale Study at Owego, New York,* EPA Project S-803618-01, July 1975

Process Design Manual for Nitrogen Control U.S. Environmental Protection Agency, Technology Transfer, October 1975

Operation Experience of Oxytanks

Skirdov, I.V., Shvetzov, V.N., Bondarev, A.A., Lurje, B.I., Bereykina, N.G., Katchkova, S.E.

The Institute VODGEO has developed a construction and a system design method for carrying out the biological wastewater treatment process of high intensity by using both pure oxygen and high concentrations of activated sludge. The system is termed "an oxytank".

The oxytank system affords achieving a high efficiency in supplied oxygen utilization, a significant reduction in total structural volume due to a combined action of biological oxidation process and mixed liquor separation in the same structural volume as well as it enables to promote the automatically controlled system for oxygen supply proportional to quantity and quality of influent wastewater.

The oxytank (Fig. 1) involves a cylindrical container inside of which a hermetically sealed reactor is positioned. (2) The reactor is provided with the surface tyrbo-aerator (5) driven in rotation by an electric motor located on the cover. The rotary hydraulic valve enables the aerator shaft to be hermetical. In the annular space between the reactor and the outside wall of the container a sludge separation tank (3) is installed where activated sludge - treated water separation has taken place. The middle part of the partition separating the reactor is equipped with ports with directed tangential nozzles (7) and with gates for mixed liquor delivery to the sludge separation tank from the reactor. The activated sludge is returned to the reactor via the annular aperture (8) in the lower part of the partition.

Thus in order to promote the intensification of sludge separation and to prevent the unwanted sludge deposits settling at the bottom of the sludge separation tank the mixing device is mounted in the form of grid with rods of 30-50 mm in diameter. The scrapers (6) are hinged in the lower part of grids. The wastewater is passed to the reactor through the pipe (1) and it is mixed with activated sludge by means of the aerator (5) then the mixed liquor is saturated with gas that is under the reactor cover. The oxygen is fed to the reactor through the pipe (9) equipped with automatic valve actuated by a pressure sensor. (12) The treated wastewater is introduced simultaneously with activated sludge to the sludge separation tank via the nozzles under the action of speed head developed by the aerator. The clarified liquor is withdrawn through the annular collecting gutter (4). The settled activated sludge is returned to the reactor through the annular aperature (8).

The given concentration of dissolved oxygen in the reaction chamber is maintained automatically. As the oxygen is being consumed by the mixed liquor the pressure of gaseous mixture in the reactor over the liquid surface decreases.

At that moment the pressure sensor (12) gives a signal for opening the valve located on the pipe (9) through which the oxygen is fed. The oxygen starts to be introduced into the system. When the gaseous mixture pressure in the reactor achieves the set level the valve automatically closes.

Gradually accumulated respirated carbon dioxide formed during the biochemical oxidation process as well as nitrogen stripped from the wastewater and also inert gases being supplied simultaneously with pure oxygen have changed gaseous mixture composition in the reactor. In this case the partial pressure of oxygen reduces while that of carbon dioxide and of other components increases. The decrease of oxygen partial pressure results in the oxygen concentration reduction in the mixed liquor and hence for the stabilization of gaseous mixture composition in the reactor it is necessary periodically to remove the accumulated gases by blowing the oxygen through the system

As the partial pressure of oxygen in gaseous mixture drops below the set level the dissolved oxygen concentration sensor (11) gives a signal for opening the automatic valve (10). The gaseous mixture from the working chamber is released into atmosphere. The oxygen is fed to the reactor through the pipe (9) instead of being withdrawn from the gaseous mixture. As the set level of dissolved oxygen concentration in mixed liquor is achieved the valve (11) closes.

On the basis of pilot plant investigations in oxytank it the method has been developed for estimation of the above type of treatment works capable to operate in a regime of reactor with complete mixing.

The wastewater retention time in oxytank reactor may be determined by the following equation

$$t = \frac{L_o - L_t}{K_{o2} K_{se} C_{se}} \qquad (1)$$

where t - average retention time for wastewater in oxytank reactor, hrs;

L_o - influent wastewater BOD fed to oxytank, mg/l;

L_t - effluent wastewater BOD, mg/l;

-specific oxygenation rate at $C_u = 3$ g/l and at oxygen concentration of 2 mg/l.

K_{O2} - coefficient with regard for the effect of dissolved oxygen concentration on specific oxygenation rate;

K sludge - coefficient with regard for the effect of activated sludge concentration on specific oxygenation rate;

'C sludge - activated sludge concentration, g/l.

The value of coefficients of both K_{O2} and K_{sludge} were experimentally defined and Figs 2 and 3 yield the corresponding curves.

The sludge separation tank design is based on determination of ultimate hydraulic load. In the course of investigations performed at the Institute VODGEO it was defined that the effect of the assumed hydraulic load on the sludge separation tank as a function of dimensionless criterion of IC.

where I - sludge index value, sm²/g;

C - activated sludge concentration in solution, g/cm³.

The curve in Fig. 4 represents this relationship. To improve the treated water quality the sludge separation tank is designed to be operated in a regime of settling tank by use of suspended solids. Special means in oxytanks allow the depth of suspended solids beds to be stabilized and ensure its exchange.

One of the oxytank features is a high oxygen concentration in the mixed liquor supplied to the sludge separation tank from the reactor. Significant store of dissolved oxygen in recycling zone of sludge separation tank combined with favourable hydrodyanamic operating conditions create provisions for intensive biochemical process in the zone. The total volume of oxytank may be divided into several zones depending on performed functions (Fig. 5).

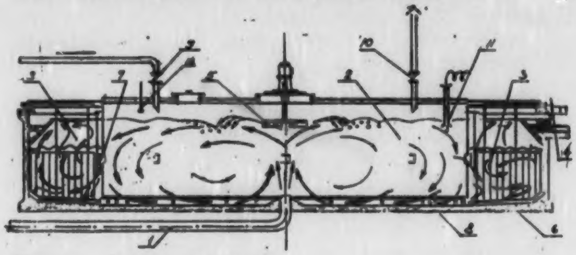


Figure 1. - Scheme of oxytank

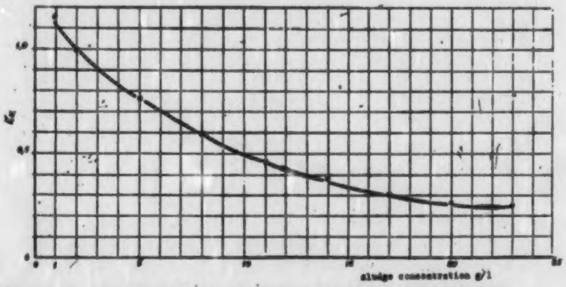


Figure 2. - Coefficient K_a VS activated sludge concentration

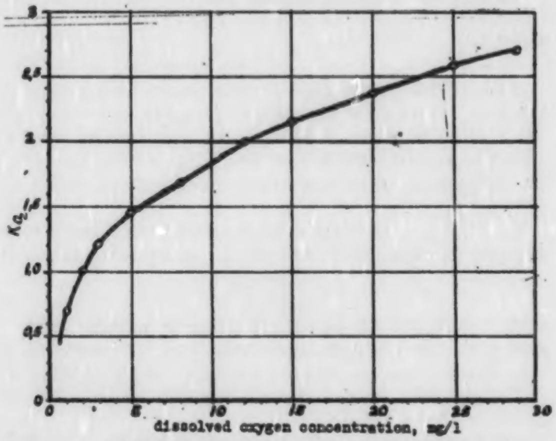


Figure 3. - Coefficient K_{O_2} VS dissolved oxygen concentration

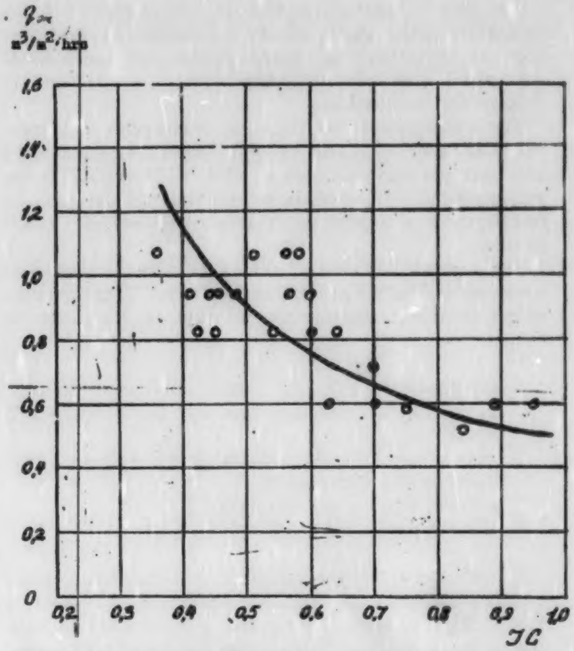


Figure 4. - Hydraulic load acting on sludge separation tank of oxytanks VS dimensionless parameter IC.

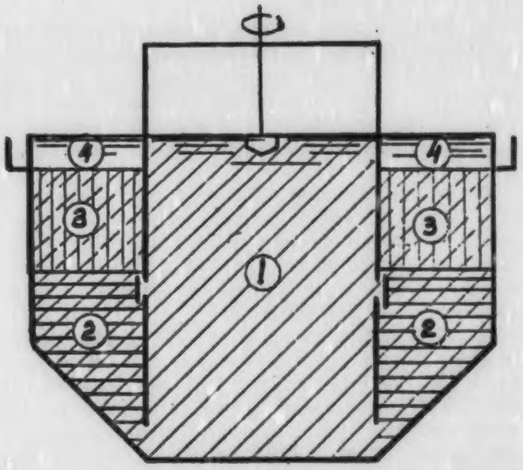


Figure 5. - Scheme of oxytank divided into the following process zones:

1. Reactor - biochemical oxidation and mixed liquor saturation by oxygen.
2. Recycle zone of Sludge separation tank - biological oxidation and mixed liquor separation.
3. Zone of suspended solids filler water treatment by filtering and oxidizing the organic compounds.
4. Protective zone.

The given scheme shows that the largest part of sludge separation tank volume in oxytank fulfils two functions such as thickening of mixed liquor and biochemical oxydation. The total structural volume is considerably reduced due to this fact.

The experimental oxytanks at wastewater treatment works of Schekinsk Combine "Azot" have been constructed and were put into operation in 1974. VNII VODGEO has recommended the oxytanks be designed on the basis of investigation of a pilot plant with a capacity of 150-200 m^3/day.

The oxytanks of volume 270 m^3 a 9.6 m in diameter each have been built at Schekinsk Combine "Azot". The following values of estimated parameters for oxytanks are presented below:

1. Oxygenation capacity (OC), $BOD_{compl.}$ - 2.04 kg/m^3/day Oxygenation capacity (OC), COD - 2.73 kg/m^3/day
2. Wastewater flow rate - 59 m^3/hr (at influent wastewater BOD of 300 mg/l)
3. Effluent $BOD_{compl.}$ - 15 mg/l
4. Effluent suspended solids - 15-20 mg/l

In order to define the actual technologic data and the sanitary efficiency of oxytank operation the Institute VODGEO in cooperation with the laboratory of treatment at Schekinsk Combine "Azot" as well as with Tula regional and Schekinsk sanitary-epidemologic stations have consistently observed these treatment works.

The average compared data of both oxytank and aeration tank operation through a long period of service are summarized in Table I.

As shown in the given results, the oxytank generation capacity was close to that estimated and exceeded 3.5 times the oxygenation capacity of full-scale aeration tanks operating in parallel at Schekinsk Combing "Azot". In this case the removal efficiency of main components from wastewater was in accordance with the complete biological treatment.

The oxytank operating efficiency doesn't practically vary at its long overload evaluated by organic impurities. So through the period of operation from March 1, to March 6, 1976 with average duration of flow retention time of 3.9 hours in reaction zone the oxytank oxygenation capacity was equal to 3720 g COD m^3/day. Over this period of time the oxytank ensured the wastewater biological treatment to be complete. Effluent $BOD_{compl.}$ was not higher than 15 mg/l, COD averaged 77 mg/l and suspended solids were maintained in amounts of 22 mg/l. With a nitrogen initial content stripped from ammoniated salts at a dose of 73 mg/l in effluent ammoniated nitrogen observed in amounts of 29.8 mg/l on average.

It should be noted that oxytank short overloads that are 1.6-1.9 times as much as the estimated loads have no adverse effect on the effluent quality.

As evidenced by the oxytank operation data which show that at the same extent of treatment the sludge index value in oxytank can be decreased 1.4-1.6 times compared to that in aeration tank.

The efficiency of oxygen usage that is supplied to oxytanks was not below 80% and averaged 93-96%.

Attention was attracted to a high concentration of ammoniated nitrogen in oxytank effluent as a result of insufficient process has taken place.

Both efficient and economical advantages of oxytanks usage may be illustrated as an example for wastewater treatment at plants of nitrogenous industry.

For economical comparison the treatment works have been taken in the following combination:

Example I - Aeration tanks with air supply by compressors.

Example II- Combined hermetical aeration tanks (oxytanks) with oxygen supply from air separation installation at the industrial plant.

The mechanical wastewater treatment works and sludge disposal plants in the given examples were accepted to be the same and because of this they are neglected in calculations.

The examples are compared by using the biological treatment plant efficiencies in the of 50,000-300,000 m^3/day.

The treatment works are designed so that complete biological treatment is ensured.

To determine the estimated parameters of aeration tanks for wastewater treatment the following performance data are used:

Influent BOD - 300 mg/l
Effluent BOD 15 mg/l
Aeration time - 16 hrs
Sludge dose - 1.5 - 3 gr/l
Aeration intensity - 4-5 m^3/m^2/hr

In oxytank calculations the retention time adopted to be 3 hours (including retention time in sludge separation tank of half an hour). An increase in oxytank capacity is caused by rise of both sludge dose up to 10-12 gr/l and dissolved oxygen concentration up to 12-14 m/l.

Technologic data from the above are considered that the compared examples are summarized in Table II.

insert table

By determining the capital expenditures for oxytank at wastewater treatment the oxygen accepted to be supplied from air separation installation. In this case the capital investment have been defined by specific investment based on cryogranic plant cost that amounted to 303 roubles/m^3/hr.

By estimating energy consumption using mechanical type aerators in oxytank the specific rate accepted to be equal

$$\frac{0.32kw.hr}{kg(O_2)}$$

with regard for an increase in aerator capacity and a decrease in energy cost respectively, therewith the oxygen was dissolved due to partial pressure elevation of this gas.

Technical-economical calculation results are summarized in Table III.

Conclusions

1. The oxytank construction is manufactured on reactor complete mixing principle and most applying to the wastewater treatment. The considered system is characterized by a high efficiency of oxygen utilization, by reducing the construction size associated with this fact that three processes such as settling, filtering through activated sludge

suspended solid bed and biochemical oxydation are combined in a sludge separation tank, as well as by automatic control system for oxygen supply that is proportional to organic impurities quantity fed with wastewater.

2. Full-scale plant studies showed that the technologic data related to oxytank performance agreed with the estimated results. In this case oxytank oxygenation capacity is 3.5 times higher compared to that for aeration tank at complete biochemical treatment of wastewater as concerns of the basic components.

3. The pure oxygen utilization affords the activated sludge concentration in oxytank to be maintained in 6-10 g/l range at high dissolved oxygen concentration of 10-12 mg/l. In so doing the settling properties of activated sludge are improved.

4. Oxytank system provided for a high quality of treated water at short overloads by 1.6-1.9 times and at long ones by 1.3-1.4 times.

Table I

Parameters	Average Month Data		Average Week Data	
	Aeration tank	Oxytank	Aeration tank	Oxytank
1. Estimated aeration time, hrs	20	5.5	20	3.9
2. Activated sludge concentration, g/l	2.5	7.8	2.5	7.4
3. Dissolved oxygen, mg/l	3-4	12	3-4	12
4. Sludge index, sm³/g	90	66		73
5. Removed BOD, %	97.4	97.4		
6. Oxygenation capacity, g COD/m³/day	743	2610	965	3720
7. Load effect on sludge, g COD/g day	298	335	302	503
Wastewater				
8. COD, mg/l	663	663	686	686
9. $BOD_{compl.}$ mg/l	487	497	512	512
10. Ammoniated nitrogen				
11. Nitrite nitrogen, mg/l				
12. Nitrate nitrogen, mg/l				
13. pH				
Treated water				
14. COD, mg/l	45	65	48	78
15. $BOD_{compl.}$, mg/l	13	13	13	13
16. Ammoniated nitrogen, mg/l				29.8
17. Nitrite nitrogen, mg/l				
18. Nitrate nitrogen, mg/l				
19. Suspended solids, mg/l	20	18	20	22

Table II *Technologic data taken from the examples I and II*

			Duration		Volume		Gas rate	
Example	Capacity	Removed BOD	Aeration	Settling	Aeration tank	Settling tank	Air	Oxygen
m³	1000 t/day	t/day	hr	hr	1000 m³	1000 m³	m³/hr	m³/hr
I	50	18.8	16	1.5	45.0	4.2	70,000	-
	100	37.6	16	1.5	90.0	8.4	140,000	-
	200	75.2	16	1.5	180.0	16.8	280,000	-
	300	113.8	16	1.5	270.0	25.2	420,000	-
II	50	18.8	3.0	1.5	8.4	4.2	-	708
	100	37.6	3.0	1.5	16.8	8.4	-	1416
	200	75.2	3.0	1.5	33.6	16.8	-	2832
	300	113.8	3.0	1.5	50.0	25.0	-	4248

5. The distinguishing feature of oxytanks is elimination of wastewater volatile components discharged into the atmosphere that prevents it from being polluted by harmful substances. At the same time if ammonium nitrogen is present in wastewater influent in large amounts because of lack of stripping the ammonia, the ammonium nitrogen content in oxytank effluent was higher than in aeration tank one.

6. Technical-economical evaluation obtained for the case of wastewater treatment of nitrogenous industry showed that the oxygen utilization in oxytanks proved to be advantageous from an economic point of view. Therewith capital investment for biological treatment works are reduced by 1.5-2 times, operating expenditures are decreased by 1.4-1.6 times and economical effect for plants with capacity of 50,000-300,000 m^3 of wastewater per day was 177,000-625,000 m^3/year respectively.

Table III

Examples	Capacity of treatment plant	Volume of aeration tanks or oxytanks	Air or oxygen rate	Capital cost				General K
				Aeration tanks or oxytanks		Air flowing and oxygen plants		
				Unit	Total	Unit	Total	
	1000 m^3/day	1000 m^3	1000 m^3/hr	roubles/m^3	1000 roubles	roubles/ m^3/hr	1000 roubles	1000 roubles
	50	45.0	70	20.4	920	-	150	1070
I	100	90	140	15.9	1430	-	190	1620
Aeration	200	180	280	14.1	2530	-	240	2770
tanks	300	270	420	13.0	3510	-	260	3770
	50	8.4	0.71	31.0	260	303	215	575
II	100	16.8	1.42	21.5	362	303	430	792
Oxytanks	200	33.6	2.73	21.5	723	303	860	1583
	300	50.0	4.25	21.5	1120	303	1290	2490

Operating costs						Biochemical treatment	Compared expenditures	Economical effect
Amortization charges			Energy cost					
Construction 3.9%	Equipment 5.3%	Total	Unit	Per year	General			
1000 roubles per year	1000 roubles per year	1000 roubles	roubles 1000m^3	1000 roubles per year	1000 roubles per year	roubles 1000 m^3	1000 roubles per year	1000 roubles per year
36.0	7.9	43.9	-	257	300.9	16.5	464	-
55.7	10.1	55.8	-	512	567.8	15.6	784	-
98.5	12.7	111.2	-	1024	1135.2	15.5	1505	-
137.0	13.8	150.8	-	1540	1690.8	15.5	2183	-
10.1	11.4	21.5	16.9	178	199.5	6.1	280	177
14.3	22.8	37.1	16.9	356	393.1	5.9	703	266
28.2	45.6	73.8	16.9	712	785.8	5.9	981	475
43.7	78.4	122.1	16.9	1070	1192.1	5.9	1540	625

Improvements for Kraft Pulp and Municipal Treatment Processes

Frank P. Sebastian
Senior Vice President
Envirotech Corporation
Menlo Park, California

Dennis S. Lachtman
Assistant to the Senior Vice President
Envirotech Corporation
Menlo Park, California

Introduction

The opportunity to reappear before such a distinguished group of Soviet and American scientists is indeed an honor. As the title suggests, my comments will be directed to process improvements in bleached kraft pulp mills, and in the municipal sector to solids processing and water monitoring. While I am not a paper expert, I am pleased to have this opportunity to present this development.

The pulp and paper industry, which has been a major contributor to both water and environmental degradation, now has some new developments that promise to reverse this trend. The Salt Recovery Process in conjunction with the closed-cycle bleached kraft mill, which will subsequently be discussed in depth, can serve as either a modification of existing facilities or an entirely new flowsheet for new or existing facilities. The closed-cycle bleached kraft mill avoids the cost of both secondary and tertiary treatment processes because it recycles materials and eliminates the need for treatment while both saving the costs of new materials and reducing water consumption.

In the municipal process area, but certainly not limited to such applications, the Hi-solids filter and control systems based on the TOC analyzer represent modifications that both enhance treatment efficiency and reduce expense.

The Hi-solids filter increases sewage sludge solids content which allows for greater energy recovery while maximizing furnace handling capability.

The TOC analyzer is a proven useful resource for quick effluent and influent monitoring and has been used to increase plant performance through a strategy of feedforward and feedback control. Where previous carbon analyzer technology was susceptable to fouling or shutdowns, new developments have all but eliminated these maladies.

Closed-Cycle Mill

One of the industries traditionally having problems with effluent streams has been the pulp and paper industry, which in the United States has recently experienced some costly and difficult years dealing with environmental control. According to *Chemical Week*(1), the paper and pulp industry paid an unprecedented $1 billion (0.756 billion Rubles) for pollution control last year. As the pulp and paper industry effluent streams approach zero discharge requirements in the United States, these costs promise to escalate further under present technology. Regardless of which country, be it the USSR or the USA, such large kinds of expenditures put a strain on production capacity.

Fortunately, there is a new and emerging process for the kraft pulp industry that promises to eliminate both contaminated effluents and the needs for external advanced waste treatment facilities. This process also reduces the cost of raw chemicals. The processes I am referring to are called the closed-cycle mill and salt control processes and were first developed by W.H. Rapson and D.W. Reeve in their research efforts at the University of Toronto(2,3). Erco-Envirotech, a joint venture of American and Canadian business interests, continued the development of the closed-cycle concept for commercial applications.

The closed-cycle mill combines a number of innovative procedures providing a process design that eliminates effluent discharges through internal recycling. The system also recovers fibers, chemicals, organics and heat normally lost to external treatment systems in conventional kraft mills.

Recognizing the obvious merits of this system a Canadian firm, Great Lakes Paper Company, has installed the first closed-cycle bleached kraft pulp mill in Thunder Bay, Ontario, Canada(4). The plant will enjoy the economic benefits to be had from eliminating waste treatment facilities, yet it will be the world's first pulp mill not to discharge contaminated effluents. The only effluent from the plant will be clean cooling water. Among the advantages that the Great Lakes Paper Company's mill will have are (5):

1. water consumption will only be 1/6 of previous levels;
2. substantial energy savings associated with heat recycle and water use reduction;
3. lower raw chemical consumption;
4. improved pulp yield, strength and brightness; and
5. elimination of need for external treatment.

Kraft Pulping and Bleaching

Before proceeding to discuss the closed-cycle kraft mill with the Salt Recovery Process, I would like to digress a moment to review the basic concepts inherent to kraft pulping.

Kraft or sulfate pulping is a process that treats wood chips with a strong alkali solution during cooking, as shown in Figure 1. The alkali solution penetrates the wood and dissolves the lignin. After cooking and washing, the end product is pulp.

The alkali solution, called white liquor, consists of sodium sulfide (Na_2S) and sodium hydroxide (NaOH). The sodium sulfide (Na_2S) serves to both speed the reaction and strengthen the pulp. Toward the end of the cook, the physical integrity of wood chips is weakened and they can be blown from the digester under pressure. The fibers are easily blown apart by steam expansion and the resultant dark-colored product is a very strong pulp, hereafter referred to as unbleached kraft pulp. The liquid fraction remaining after the cook is black and it contains more than half the original wood content in addition to spent chemicals(5).

The kraft process must recover this black liquor to be economically efficient. The box marked "Black Liquor Evaporator" in Figure 1 is where the black liquor, after being washed from the brown pulp in the preceding box marked "Brown Stock Washing" is concentrated via evaporation. The concentrated black liquor is burned in a furnace and the remaining smelt is dissolved in water. This solution contains sodium carbonate (Na_2CO_3), and sodium sulfide (Na_2S) and is referred to as green liquor. The sodium carbonate (Na_2CO_3) is then causticized with lime. This last step is schematically shown in Figure 1 as occurring in the box marked "Liquor Preparation." The resultant solution, which is clear and called white liquor, is reused for pulping.

The kraft mill is not a major pollutant process, as 95% of the chemicals are continuously reused in the described flowsheet. However, the brown-colored pulp is not as desirable nor does it command as high a price as bleached pulp.

Early attempts to bleach brown pulp with chlorine (Cl_2) and caustic soda led to substantial strength losses. However, bleaching with chlorine dioxide (Cl_2O), chlorine (Cl_2) and sodium hydroxide (NaOH) make it possible to get pulp brightness of 88-92% G.E. without losing pulp strength. This development which was also pioneered by Dr. Rapson, led to a large worldwide expansion of kraft pulp production(5).

The bleaching plant contributes the major pollutant burden from bleached kraft mills. Bleaching dissolves another 7-10% of the pulp which in combination with spent chemicals and toxic compounds like chlorophenols comprise the bleaching plant effluent. Since this effluent can be very toxic, the closed-cycle bleached kraft mill concept is a significant development, both economically and environmentally. I will be discussing the detailed economic advantages of the closed-cycle mill in a following section.

The Process at Great Lakes Paper Company Thunder Bay, Ontario, Canada

The plant scheduled to start up late this year will produce 250,000 tons (227,000 metric tons) per year of bleached market grade pulp. Many of the process techniques for this plant have either been demonstrated or are being used in mills throughout the world today. Those process techniques already used elsewhere and contained in the Thunder Bay flowsheet are the following(6):

1. Countercurrent washing in the bleachery:
2. high chlorine dioxide substitution for chlorine in the first bleaching stage;
3. steam stripping of contaminated condensate; and
4. a closed screen room; and
5. spill tanks to accommodate temporary process upsets and allow subsequent recycle.

The unique aspect of the Thunder Bay flowsheet is the total recycle of bleachery effluent, as shown in Figure 2, to the unbleached portion of the mill. Normally, the problem with such a recycle procedure would be the build-up or introduction of sodium chloride, which must be removed at the same rate it is introduced. To remedy the situation, the Erco-Envirotech SRP (Salt Control Process) System will be used.

Salt Control Process

The SRP System is schematically represented in Figure 3. Basically, the process uses white liquor from the liquor preparation section of the mill and treats it in a two-stage evaporization and crystallization procedure where sodium chloride is purified for reuse and sodium carbonate (Na_2CO_3) and sodium sulfate ($NaSO_4$) are recycled back to recovery and recausticizing.

The white liquor fed into stage one is 2-3% by weight sodium chloride (NaCl) and 10-11% by weight consists of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). As shown in Figure 4, a triple set of evaporators using backward feed concentrate the liquor to approximately 26% by weight sodium hydroxide (NaOH) plus sodium sulfide (Na_2S). All three evaporators are forced-circulation units having external heat exchangers. The final liquor temperature is between 250 and 260° F(6).

In the evaporators, sodium carbonate ($NaCO_3$) and the double salt burkeite (Na_2CO_3-$2Na_2SO_4$) will crystallize out of solution. A clarifier removes these crystals and a rotary vacuum drum-filter further dewaters these crystals. Most of these crystals are recycled to the liquor preparation or recausticizing section and a small quantity is sent, as needed, to the furnace for the purpose of reducing sulfates (SO_4) to sodium sulfide (Na_2S). The filtrate from the rotary vacuum drum filter is recycled back to the first evaporator.

The concentrated liquid leaving the clarifier in step 1 enters an evaporator-crystallizer in step 2 and is further concentrated to approximately 36% by weight sodium hydroxide (NaOH) and sodium sulfide (Na_2S). At this point most of the sodium chloride crystallizes out of solution.

The sodium chloride (NaCl) crystal slurry enters another clarifier unit where a concentrated white liquor is removed. This white liquor contains only trace quantities of sodium chloride (NaCl), sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4), but has all the active alkali for pulping. The stage 2 clarifier underflow is pumped to another rotary vacuum drum filter for crystal dewatering. These crystals are further purified via an agitated leach tank, where residual amounts of sodium carbonate (Na_2CO_3) and burkeite (Na_2CO_3-$2Na_2SO_4$) are dissolved. The slurry is fed to a horizontal vacuum belt-filter, where a countercurrent washing process yields a better than 99% pure sodium chloride (NaCl) cake. As will be mentioned later, the pure sodium chloride (NaCl) cake can serve as a raw material for the manufacture of chlorine dioxide (ClO_2) in the bleaching process or it may be used as a resource having an average selling price of 0.64¢/lb. (1 Kopeck/kg). The consumed salt (NaCl), has numerous uses including the salting of roads.

The filtrate from the rotary vacuum belt filter is partially recycled to the leach tank and the remainder passes to the third stage evaporator of the stage-one evaporation system.

Economics

Having discussed the details of the closed-cycle bleach kraft mill system with the SRP System, I believe it is established that this system would clearly be the method of choice from an environmental standpoint. However, in the U.S. and most likely for the U.S.S.R. as well, economic pressures are critical parameters for the choosing of such systems or flowsheets.

Figure 5 illustrates a theoretical model of a 900 short ton per day (TPD) (818 metric tons/day) coniferous bleached pulp producing plant similar to the Thunder Bay flowsheet(7). The data in Figure 5 show the estimated annual savings in operating costs for the closed cycle mill in comparison to kraft mills not utilizing the following:

1. Salt Control Process:
2. counter current washing;
3. high substitution of chlorine dioxide (ClO_2) for chlorine in the first stage of the bleachery;
4. steam stripping of condensate; and
5. closed screen room and spill tanks that accommodate process upsets; and
6. recycle of all bleachery effluent within the mill.

The total savings from operating costs which are in excess of $5,000,000 (3,785,000 Rubles) are approximately one-half the capital costs. Additionally, these statistics exclude such factors as the value of salt (NaCl) recovered or the potential value of heat that could be recovered from the clean cooling water make-up. The value of the salt (NaCl) for a 900 TPD (818 metric tons/day) plant would be $224,000 per year (169,344 Rubles/year). The value of heat recovery would vary depending on the climate, but would be of greatest value in colder climates like those characteristically found in many parts of Russia, where such thermally enriched waters can be used for building heat. Appendix 1 contains the detailed analyses for the cost savings statistics as contained in Figure 5.

Recent statistics for the Thunder Bay installation show that the 250,000 ton per year (227,000 metric tons/year) facility (Figure 6) will save approximately $4,000,000 (3,024,000 Rubles) annually(8). This saving originates from modifications that improve its performance over a conventional mill in the following areas:

1. Reduction of fresh water usage from 25,000 (95 cubic meters/1000 kg) to 4,000 gallons per ton (64 cubic meters/1000 kg) of pulp,
2. net energy savings of 5,000 lbs. (2500 kg) of steam per ton (1000 kg) of pulp, and
3. savings from reduced consumption of raw chemicals.

Since the differential cost of this closed-cycle and that of a conventional mill is $8,000,000 (6,048,000 Rubles), the payback or break even period is approximately two years. Whereas conventional primary, secondary and tertiary wastewater treatment facilities do not normally bring in a return of economic benefit to the plant, the closed-cycle mill with the SRP System, which is less costly than these external waste treatment systems, has the advantage of paying for itself within a remarkably short time period.

According to the Environmental Protection Agency (EPA)(9), the 1975 U.S. production capacity for all kinds of pulp was 96,000 metric tons per day. The largest single pulp process used is the kraft process, which produced 72,379 metric tons per day or 75.4% of the U.S. pulp supply in 1975. The EPA reports that kraft pulp mills will need to spend $895,000,000 (677 million Rubles) to meet best practical technology (BPT) and $732,000,000 (553 million Rubles) for best available technology (BAT) effluent guidelines as required by the EPA(10).

In light of the large investments necessary for complying with EPA effluent guidelines and the large percentage of pulp production potentially effected, the closed-cycle mill should have significant economic benefit for the U.S. pulp industry. In addition, the closed-cycle mill provides the best solution environmentally. This process should also prove to be similarly beneficial for other countries having kraft mills that desire to improve their effluent streams while simultaneously recovering investment capital.

Hi-Solids Filter

In the area of municipal treatment, I would like to discuss the Hi-Solids filter, a newly developed sludge dewatering process. Basically, the Hi-Solids filter is similar to a combination of vacuum filtration followed by filter pressing.

The Hi-Solids system was designed to both reduce fuel consumption for sludge incineration and pyrolysis systems requiring auxiliary fuel and increase energy recovery in those sludge incineration and pyrolysis systems where recovery of excess heat is possible.

Reducing Furnace Fuel

With incineration and pyrolysis sludge furnaces, fuel consumption is directly proportional to both the volatile and moisture content of the sludge. This relationship is illustrated in Figure 7. Notice how energy consumption decreases proportionately to the reduction in sludge moisture. As the sludge volatile content increases, the fuel requirements approach zero and eventually reach the point of negative fuel value or energy recovery. I will discuss energy recovery in more detail in the following section.

Performance data from a pilot Hi-Solids unit in Hatfield, Pennsylvania (see Figure 8) shows that sludge from that treatment facility was dewatered to 32.8% volatile solids compared to the previous 20.2% sludge solids content achieved by conventional drum-filter dewatering.

In terms of fuel savings, the Hi-Solids filter can reduce sludge furnace fuel consumption substantially. For example, the data in Figure 9 show that utilization of a Hi-Solids versus a vacuum filter would reduce fuel costs by $70,000 (52,920 Rubles) annually or 32% in a MHF sludge furnace handling 5000 metric tons of dry sludge solids yearly.

Since the Hi-Solids filter increases the sludge volatile content by 35-40% over vacuum filters and up to 50% over that from drum filters, this represents a large monetary value to be accrued from this energy saving.

Increased Energy Recovery

In a number of U.S. sewage treatment plants (see Figure 10), sludge incinerators using waste heat recovery methods collect excess process heat. In such systems, this energy can be utilized to offset the power requirements needed to run other parts of the treatment plant. In such installations, the increased sludge dewatering capability of the Hi-Solids filter could provide sizeable savings by reducing fuel consumption.

The dewatering capability for the Hi-Solids filter largely depends upon the type of sludge. In Figure 11 the predicted performance capability for various types of sludge handled by this filter are given. The 18-55% variation in sludge dry solids content spans the benefits of reducing fuel consumptions in furnaces burning sludges with solids content requiring auxiliary fuel to increasing the amount of energy recovered in furnaces handling sludges having solids content surpassing the (25% in the MHF) autogenous fuel sludge solids content.

TOC Analyzer

Another innovation that can be used for improving municipal treatment efficiency is the total organic carbon (TOC) analyzer. The importance of this instrument has increased in the United States since recognition of the link between trace organics and cancer in humans. Accordingly, sewage treatment facilities are starting to place more emphasis on reducing organic and trace organic effluent streams loadings.

Whereas BOD_5 has been and should remain a useful indicator of water quality, the TOC measurement gives a more detailed and rapid assessment of organic loadings that can be used to modify and optimize treatment efficiency. While BOD_5 measurements take five days to complete, TOC data is ready in a matter of minutes. Measurement of total organic carbon at various points in a treatment plant can provide timely and valuable operating information. This is especially true when operating activated sludge processes.

Optimization of Sludge Treatment

The TOC analyzer is an effective test for controlling activated sludge processes. The TOC can be used to implement two popularly used design approaches for activated sludge systems. The first uses a food to microorganism (F/M) ratio and relies on the observation that the amount of biodegradable organics applied to biological systems affect the microorganism metabolic rate(12). The other popular design approach uses the principle of biological growth rate in relationship to substrate concentration as a model to control process performance. Lawrence and McCarty have used this model for sludge retention time (SRT) design(12). In their technique, SRT is the inverse of the biological growth rate. The SRT is espoused as a comprehensive basis for biological design because all process variables can be related to it. The SRT process is controlled by sludge wasting.

While opinions may vary as to the efficiency of using either or both the F/M ratio or the SRT process control strategy, TOC measurements apply to both process control strategies.

TOC measurement might be taken in the activated sludge process at various stages (see Figure 12). For example, using the TOC values from raw sewage and comparing this to TOC values after primary treatment can be used to evaluate the effectiveness of the primary settling process.

The collecting of samples at either of the above two points poses problems in regard to representative or truly random sampling. To alleviate these difficulties, laboratory models use blenders and homogenizers. For treatment plants using on-line measurements, commercial grade grinding pumps homogenize the sample particles before analysis. In either case, good TOC analyzers are specifically designed to handle such samples.

The mechanisms for TOC feedforward and feedback control strategies would be implemented after making various changes depending on the design characteristics being followed.

For example, F/M ratio control can be effected by measuring TOC for primary effluent, TOC_{PRI}, and for return activated sludge, TOC_{RAS}. The F/M ratio can then be calculated as follows:

$$\frac{F}{M} = \frac{\text{Primary Flow (Vol/Time x } \text{TOX PRI (Wt/Vol)}}{\text{RAS FLOW (Vol/Time x } TOC_{RAS}\text{ (Wt/Vol)}}$$

$$= \frac{\text{Wt. of Primary Organics}}{\text{Wt. of RAS Organics}}$$

Adjustment of RAS flow can be applied to maintain a constant F/M ratio. Sludge retention time can be controlled by regulating the sludge inventory of the plant since,

$$SRT = \frac{\text{Biological Mass in System}}{\text{Biological Mass wasted/time}}$$

TOC measurement of mixed liquor leaving the aerator, TOC_{MG} and TOC_{RAS} can be used in combination with plant volumetric data to calculate the organic mass in the system. This data can then be utilized to adjust the plant wasting rate.

Alternately, TOC_{PRI} - TOC_{SEC} (TOC of secondary or final effluent) can be used to calculate the quantity of new sludge made. This data can be used to adjust the plant wasting rate and thus utilize SRT control. This technique assumes that (k) is constant in the following relationship:

$$\text{New Sludge} = k\,(TOC_{PRI} - TOC_{SEC})$$

Finally, TOC_{SEC} can be employed as a final indication of plant effectiveness. While the quality of effluent water from a waste treatment plant is usually evaluated by the BOD_5, TOC values are an equally useful monitoring tool. If the effluent TOC values are maintained as low as are economically feasible, the BOD_5 values will also be as low as are economically feasible.

The Hillsboro Story

Although many sewage treatment plants use TOC analyzers to monitor and aid in optimizing their treatment efficiency, one case stands out above the rest as an illustrative testimony for the TOC analyzer. This example involves the Hillsboro, Oregon Waste Treatment Facility that was put on line in March 1971(13). Due to high and varying organic loadings from the local food industry, the Hillsboro plant was operating below the effluent standards set forth by Oregon's Department of Environmental Quality (see Figure 13). At times the wastes from local industries comprised 75% of the plant's organic loading. Organic loadings have and will vary up to 50%.

In July of 1973, a new strategy was initiated which relied upon fast measurement and control of key plant variables. The following measurements routinely measure and controlled for were the following:

1. F/M ratio,
2. respiration rate of aeration tank effluent,
3. 5-minute settling of aeration tank effluent, and
4. dissolved oxygen in aeration tank.

The adjusted parameters to improve performance efficiency were:

1. returned sludge flow,

2. waste sludge flow,
3. sludge conditioning time, and
4. aerator air flow.

The results of this new strategy have proven extremely successful. Figure 14 shows that the Oregon plant had BOD$_5$ average from 20-90mg/liter prior to adoption of the new strategy. Following institution of the new strategy, the plant was able to consistently meet the Oregon effluent standards as the BOD$_5$ dropped to between 10 and 15 mg/liter on a monthly average (see Figure 14).

This is one working example of the TOC analyzer and its useful application for controlling efficiency in municipal waste treatment processing plants. Many other applications for the TOC analyzer are employed as it is widely used by American industry, which has traditionally accounted for the largest sector of the TOC analyzer production output. Whether the TOC analyzer be used as a laboratory or continuous in-line device, the results and application potentials remain the same; only the means of sampling changes.

Summary

In conclusion, I have discussed three treatment modifications that have the advantages of improving treatment efficiency and reducing costs.

The closed-cycle mill, which can be a modification of existing kraft pulp plants, totally eliminates contaminated effluents while saving enough through operating expenses to recover its initial capital expenditures in a two year period. After the two years of operation, the closed-cycle mill continues to generate these savings as revenue - a prospect that external waste treatment facilities cannot offer.

The high-solids filter has application for both municipal and industrial sludge processing. This new development is a modification in sludge processing that promises to reduce energy consumption and increase energy recovery in sludge thermal systems.

The TOC analyzer also has applications for both industrial and municipal treatment processes. Although no examples of industrial uses were given, the product is most widely purchased for industrial applications. The TOC analyzer has the advantage of being a reliable and quick measurement tool that has found application in improving waste treatment efficiency through a network of feedforward and feedback control strategies in addition to its general application as a monitoring device.

Bibliography

1. *Papermakers Face More Pollution Woes, Chemical Week,* p 35, May 5, 1976.
2. *TAPPI Medalist, Tappi,* 58:12, p 3, December 1975.
3. Stevens, F., *First Pollution Free Bleached Kraft Mill Gets Green Light,* Pulp and Paper Canada, 76:10, p 27, October 1975.
4. *Rapping With Rapson,* Pulp and Paper, October 1973.
5. Emmerson, D. W., *The Long Hard Road To The Effluent-Free Mill,* Chemistry In Canada, p 11, April 1976.
6. Cornell, C.F., *Salt Recovery Process Allows Reuse of Pulp-Bleaching Effluent,* Chemical Engineering, p 136, November 10, 1975.
7. Rowlandson, G., *Economic Advantages of Closed-Cycle Mill,* Erco-Envirotech Study, December 15, 1975.
8. "Zero Pollution From A Paper Pulp Process," *Business Week,* p 48, December 22, 1975.
9. *Development Document for Interim Final and Proposed Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Bleached Kraft, Groundwood, Sulfite, Soda, Deink and Non-Integrated Paper Mills, (Vol. 1) Segment of the Pulp, Paper and Paperboard Point Source Category,* United States Environmental Protection Agency, p 31, January 1976 (EPA 440/1-76/047-a).
10. *Economic Analysis of Proposed and Interim Final Effluent Guidelines for the Bleached Kraft, Groundwood, Sulfite, Soda, Deinked and Non-Integrated Paper Sectors of the Pulp and Paper Industry,* United States Environmental Protection Agency, p 12, January 1976, (EPA-230/2-76-045).
11. *State of the Art Review on Sludge Incineration Practice,* U.S. Department of Interior 17070 Div. 04/70.
12. Stensel, H. D., Shell, G. L., *Two Methods of Biological Treatment Design, JWPCF* 46(2), p 271, February 1974.
13. Joyce, R. J., Ortman, C., and Zickefoose, C., *Optimization of An Activated Sludge Plant Using TOC, Dissolved Oxygen, Respiration Rate and Sludge Settling Volume Data,* Presentation before WWEMA Industrial Water and Pollution Conference, Detroit, Michigan, April 1, 1974.

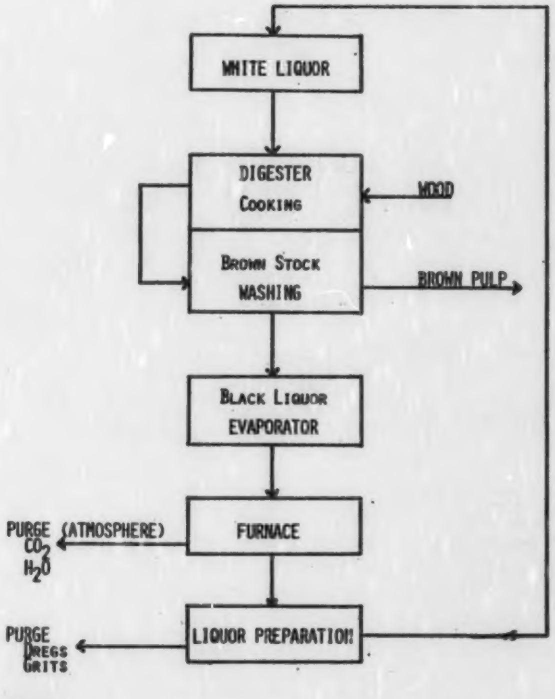


Figure 1

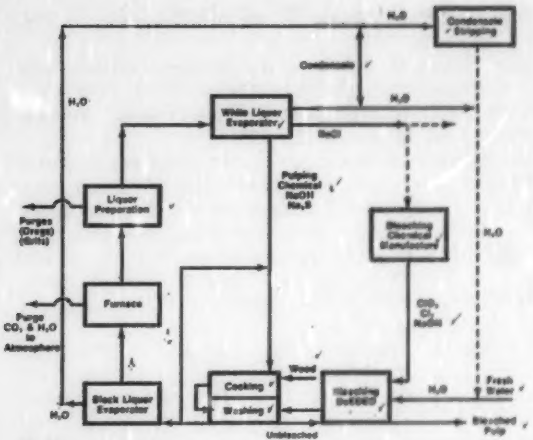

H₂O
Condensate Stripping
Condensate
H₂O
White Liquor Evaporator
H₂O
NaCl
Pulping Chemical NaOH Na₂S
Liquor Preparation
Purges (Dregs) (Grits)
Bleaching Chemical Manufacture
H₂O
Furnace
Purge CO₂ & H₂O to Atmosphere
ClO₂ Cl₂ NaOH
Wood
Cooking
Washing
Bleaching
H₂O
Fresh Water
Black Liquor Evaporator
H₂O
Unbleached Pulp
Bleached Pulp

Figure 2

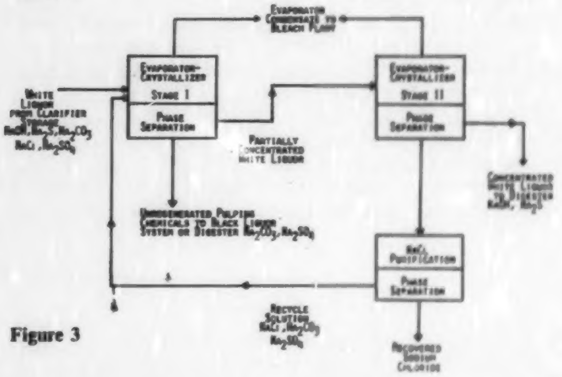

Evaporator Condensate to Bleach Plant
Evaporator-Crystallizer
Stage I
Phase Separation
Evaporator-Crystallizer
Stage II
Phase Separation
White Liquor from Clarifier Storage NaOH, Na₂S, Na₂CO₃ NaCl, Na₂SO₄
Partially Concentrated White Liquor
Concentrated White Liquor to Digester NaOH, Na₂S
Unregenerated Pulping Chemicals to Black Liquor System or Digester Na₂CO₃, Na₂SO₄
NaCl Purification
Phase Separation
Recycle Solution NaCl, Na₂CO₃ Na₂SO₄
Recovered Sodium Chloride

Figure 3

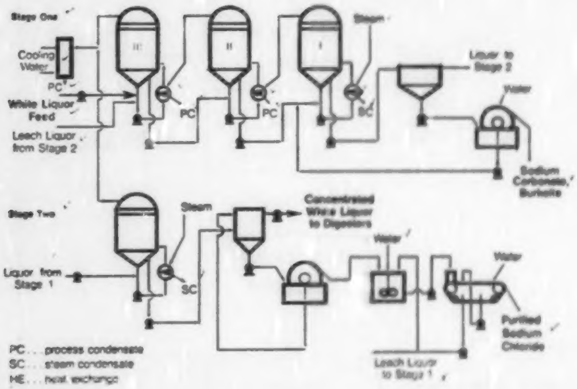

Stage One
Cooling Water
PC
White Liquor Feed
Leach Liquor from Stage 2
III
II
I
Steam
PC
PC
SC
Liquor to Stage 2
Water
Sodium Carbonate, Burkeite
Stage Two
Steam
Concentrated White Liquor to Digesters
Water
Water
Liquor from Stage 1
SC
Purified Sodium Chloride
Leach Liquor to Stage 1
PC . . . process condensate
SC . . . steam condensate
HE . . . heat exchange

Figure 4

Estimated Annual Operating Cost Savings Closed-Cycle Mill Salt Recovery Process
(Calculated to Nearest Thousand)

	Dollars	Rubles
1. Heat Savings		
A. Decreased Steam Consumption	$ 839,000	634,284
B. Additional Steam Production from Reclaimed Organics	$ 271,000	204,876
2. Fiber Savings	$ 776,000	586,656
3. Yield Increase	$ 636,000	480,816
4. Chemical Savings	$1,189,000	898,884
5. Water Savings	$ 68,000	51,408
6. Savings in Effluent Treatment Cost	$1,584,000	1,197,504
	$5,363,000	4,054,428

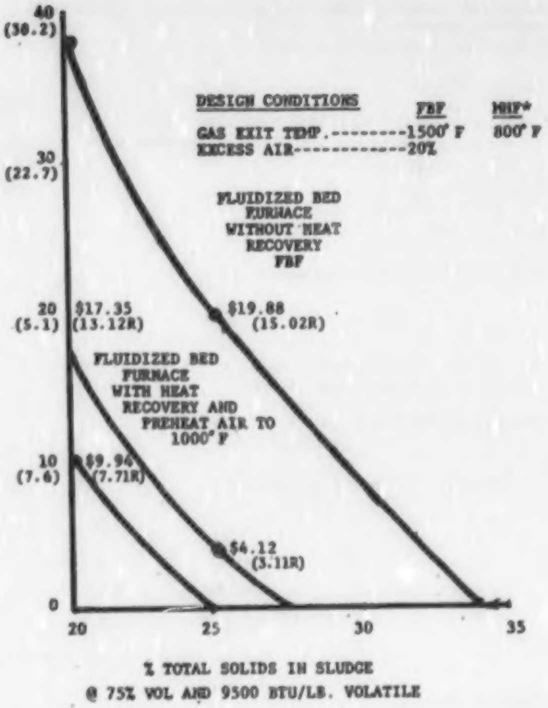
Basis: 900 TPA (409,000/day) Coniferous Pulp - KAPPA No. 32
Bleached Pulp Brighiness - 90 (G.E.)

Figure 5

Capital and Operating Costs

Mill Capacity	-	700 A.D. tons per day (636,000 kg per day)
White Liquor Use	-	130 ft³ per ton pulp
Active Alkali	-	793 lbs Na₂0 per ton pulp (324 kg per 1,000 kg pulp)
Sodium Chloride Recovered	-	120 to 200 lbs NaCl per ton pulp (54.5 to 90.9 1,000 kg)
Capital Cost		$8,000,000 (6,048,000 Rubles)
Utilities		
Steam		96,000 lbs per hour (43,636 kg/per hour)
Power		875 H.P.
Water		6,000 G.P.M (surface condenser)
Raw Materials:		None

Figure 6



* Multiple Hearth Furnace - 22' dia.; 6 hearths
Source: (11) and Envirotech data

Effect of moisture content on the cost of sludge combustion systems with and without heat recovery

Figure 7

Performance summary
Hatfield, Pennsylvania

Filter Type	Production (Kg DS/hr-sq m)	Filter Cake DS-%	Kg H20/Kg DS
Drum	6.8	20.2	3.95
Hi-solids	9.1	32.8	2.05

Figure 8

Incineration Fuel Comparison

Dry sludge solids	Vacuum filter	Hi-solids filter
Per year; metric tons	5000	5000
Cake; % ds	20	27
Gross Heat required;		
Billions BTU per year	108	73.0
Fuel cost 2.0 U.S.	216,000	146,000
Dollars per million BTU:		
U.S. dollars per year		
Rubles per year	163,296	110,396

32% FUEL SAVINGS

Figure 9

Sewage treatment plant locations with sludge energy recovery systems
(United States)

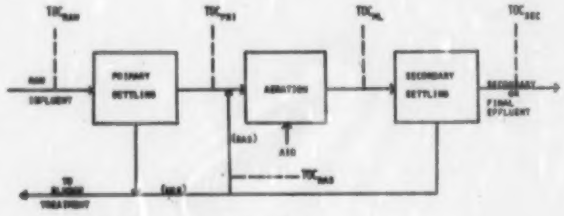
1. Central Contra Costa Sanitation District, California
2. Jacksonville, Florida
3. Granite City, Illinois
4. Western Branch Facility, Prince Georges County, Maryland
5. Atlantic County, New Jersey
6. Trinity River Authority, Texas
7. Hatfield, Pennsylvania
8. Chesapeake-Elizabeth-Hampton Roads Sanitation District Virginia,
9. Hopewell, Virginia
10. Green Bay, Wisconsin

Figure 10

Hi-solids filter capability

Sludge type	Production (Kg DS/hr-sq m)	Filter cake DS-%	KG H20/Kg DS
Raw Primary	25-50	30-40	1.5-2.3
Waste activated	7-10	18-20	4.0-4.6
Raw primary plus waste activated (50:50 by weight)	10-15	24-28	2.6-3.2
Raw primary plus humus (50:50 by weight)	15-20	25-27	2.7-3.0
Heat treated raw primary plus waste activated	15-25	45-55	0.82-1.2
PCT (lime)	10-20	30-35	1.9-2.3

Figure 11



WAS = waste sludge flow
RAS = return sludge flow
TOC RAW = TOC of raw influent
TOC PRI = TOC of primary effluent
TOC ML = TOC of mixed liquor leaving aerator
TOC SEC = TOC of secondary of final effluent
TOC RAS = TOC of return activated sludge

Figure 12

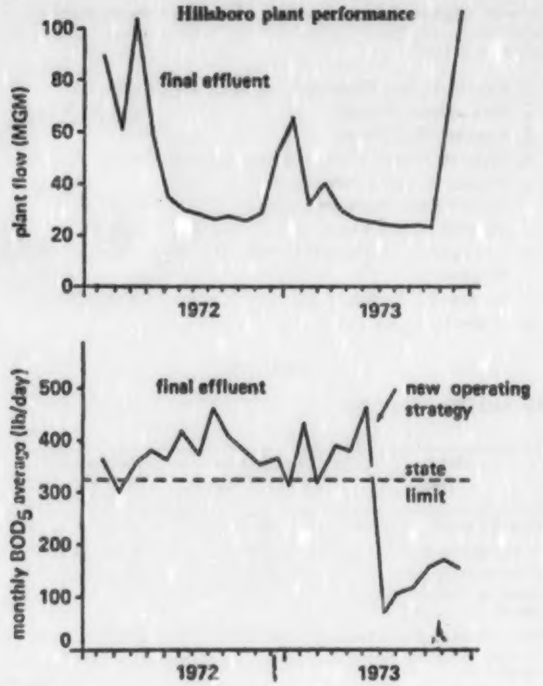


Figure 13

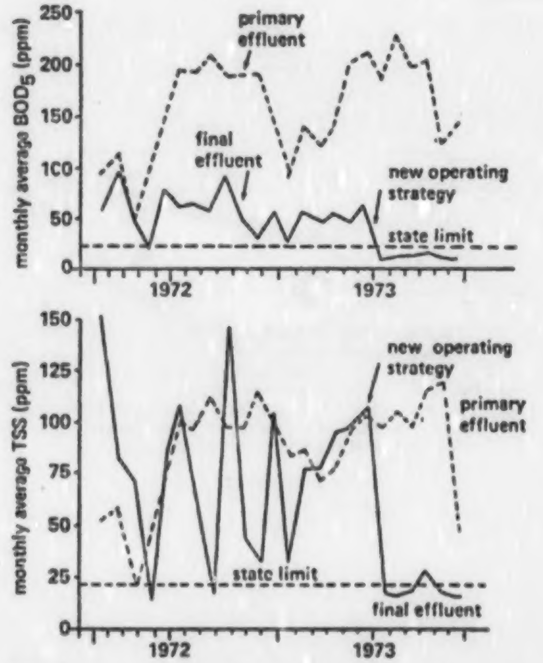


Figure 14

Appendix 1(7)

Estimated annual operating cost savings closed-cycle mill salt recovery process
(Calculated to Nearest Thousand)

1. Heat Savings	
A. Decreased Steam Consumption	$ 839,000
B. Additional Steam Production from Reclaimed Organics	$ 271,000
2. Fiber Savings	$ 776,000
3. Yield Increase	$ 636,000
4. Chemical Savings	$1,189,000
5. Water Savings	$ 68,000
6. Savings in Effluent Treatment Cost	$1,584,000
	$5,363,000

BASIS: 900 TPD Coniferous Pulp - KAPPA No. 32
Bleached Pulp Brightness - 90 (G.E.)

CONIFEROUS PULP—900 T/D - 345 D/YR
—310,500 T/YR

(1) Bleachery Sequences C-E_1-D_1-E_2-D_2

Stage	C	E	D
1	6.5%	0	0
2	0	4.50%	0
3	0	0.20%	1.0%
4	0	0.50%	0
5	0	0.05%	0.5%
	6.5% (130#)	5.25% (105#)	1.5% (30#)

Chemical Balance:
1# Chlorine Requires 1.13# NaOH
1# Chlorine Dioxide requires 0.60# of NaOH
∴Checking Cl- and Na+

Chloride (Caustic)
1st Stage C = 6.5% = 130#/T = 130 x 1.13 = 146.9
3rd Stage D_1 = 1.0% = 20#/T = 20 x 0.6 = 12.0
5th Stage D_2 = 0.5% = 10#/T = 10 x 0.6 = 6.0
Total caustic required (for "balance") = 164.9#/T

NOTE: All units are U.S., i.e. tons are short tons (2000 lbs).

Sodium
2nd Stage (E_1) = 4.50% = 90.0# (1st extraction)
3rd Stage = 0.20% = 4.0# (buffer-pH control)
4th Stage (E_2) = 0.50% = 10.0# (2nd extraction)
5th Stage = 0.05% = 1.0# (pH control)
Caustic added in bleach plant = 105#
∴additional caustic to "balance" = 164.9 - 105 = 59.9#/T. This amount must be added to the mixed filtrate for link-up of Cl- and Na+ (as NaCl) and need for pH adjustment.

Sodium Chloride Load:

Stage	Chlorine	Chlorine Dioxide
1	130.0	0
3	0	10.5
5	0	5.2
	130.0	15.7

Total chloride = 145.7
∴Total sodium chloride load (as NaCl)

$$= 145.7 \times \frac{58.5}{35.5} = 240\#/T$$

Total dioxide needed = $\frac{1.5}{100} \times 900$ = 13.5 T/D

(2) Bleachery Sequence D/C-E_1-D_1-E_2-D_2

(Based on 70% substitution with chlorine dioxide in the first stage)

—30% as Cl_2 = 1.95% = 39.0#/T
Chloride Load = 39.0#/T
—70% of total Cl_2 demand as dioxide
ClO_2 as Cl_2 = 0.7 x 6.5 = 4.55%
as ClO_2 = $\frac{4.55}{2.63}$ = 1.73% = 34.6#/T

Chloride load = 34.6 x $\frac{35.5}{67.5}$ = 17.9#/T

Total chloride (Cl-) load = 39.0 + 17.9 + 10.5 (D_1) + 5.2 (D_2) = 72.6
Sodium chloride (NaCl) load
= 72.6 x $\frac{58.5}{35.5}$ = 120#/T

Balancing Cl- and Na + (actual NaOH = 81#/T)

Caustic Requirement:

Stage	Chlorine (as NaOH)	Caustic	Dioxide (as NaOH)
1	39.0 x 1.13 = 44.10	—	34.6 x 0.6 = 20.76
2	—	64	—
3	—	6	20 x 0.6 = 12.00
4	—	10	—
5	—	3	10 x 0.6 = 6.00
	44.10	83#	38.76

Caustic requirement = 44.10 + 38.76 = 82.86#/T
∴Cl- and Na+ are balanced (NaCl)
Total dioxide needed
= [1.73% $\frac{+ 1.0\%}{100}$ + 0.5%] x 900
+$\frac{3.23}{100}$ x 900 = 29.07 T/D

(3) Basic Data

(a) Costs

Chlorine	6.5¢/lb.
Caustic Soda	7.0¢/lb.
Chlorine Dioxide	24.0¢/lb (R3)
Wood	$40/cord (2.25 cords/T)
Unbleached Fiber	$150/Ton
Fiber in process	$195/Ton
Pulp "semibleached"	$250/Ton
Bleached Pulp	$360/Ton
Steam	$2.25/M lbs. (Total Cost)
Water	2¢/M Gals (Incl power, labor & treatment)
Effluent and Emmissions	$7/Ton (OECD, Ekono) (For primary & secondary)

(b) Operating days per year 345

(c) Bleachery Chemical shrinkage 6%
(Minimum of one (1) percentage point yield gain due to high substitution with ClO_2 for Cl_2 in the 1st stage.)

(d) Bleachery fiber *loss* 1% (average - with conventional "C" and "E_1" filtrates sewered)

(4) Estimated Savings ** Per year (D/C-E_1-D_1-E_2-D_2)

(A) Steam Consumption

The decreased amount of steam due to: lower water volume used, countercurrent reuse of filtrates, modified concentrations of bleach solutions, etc., is approximately 130,000#/Hr. The steam required to concentrate the mill white liquor in the SRP in order to remove the salt load is approximately 85,000#/HR (quadruple effect).

∴ Differential 130,000 - 85,000 = 45,000#/Hr
Savings = 45,000 x $\frac{2.25}{1,000}$ x 24 x 345 = $839,000/yr.

(B) **Steam Production (Higher Organics 54T/D)**

Bleachery shrinkage 6% overall—recovery boiler (steam) efficiency 65% [decreased inorganics—sodium carbonate, sodium sulfate (as well as make-up salt cake) considering salt input] recovered organic solids heating value 5,000 + B.T.U./lb.

Savings = 0.06 x $\frac{310,500}{1,000,000}$ x 2,000 x 5,000 x 2.25 x .65
= $271,000/yr.

(C) **Fiber Loss Decreased** ("average" pulp price $250/Ton as fiber not completely processed—bleached nor dried)

Elimination of fiber loss from dryer, bleachery, screening and washing departments means an "average" fiber gain of $\frac{1.00}{100}$ x 900 = 9.0 T/D. This pick-up increases pulp production—decreases chemical usage—or mill may choose depending on boiler capacity, etc., to decrease amount of wood cooked (lower overall and organic load to the recovery boiler).

Savings = 9.0 x 250 x 345 = $776,000/yr ("Increase Income")

(D) **Yield**

Due to the high substitution (70%) with chlorine dioxide in the first stage (since it will be operated "HOT") there is a yield improvement of at least one (1) percentage point when compared to a hot chlorination sequence. This enhancement due mainly to the protection of the hemicelluloses will coincidentally decrease other associated processing charges so that an overall cost advantage of at least $2.05/T may be realized.

Savings = 2.05 x 310,500 = $636,000/yr.

(E) **Bleaching Costs**

** (i) For the sequence C-E_1-D_1-E_2-D_2 the chemical consumptions are:

Chlorine = 130#/T at 6.5¢/lb = $ 8.45
Caustic Soda = 165#/T at 7.0¢/lb = $11.55
Chlorine Dioxide = 30#/T at 24¢/lb = $ 7.20
Total Chemical: $27.20

(ii) For the sequence D/C-E_1-D_1-E_2-D_2 the chemical consumptions are:

Chlorine = 39#/T at 6.5¢/lb = $ 2.34
Caustic Soda = 83#/T at 7.0/lb = $ 5.81
Chlorine Dioxide = 62.6#/T at 24¢/lb = $15.02
Total Chemicals = $23.37

Differential = 27.20 - 23.37 = $3.83/T
Savings = 310,500 x 3.83 = $1,189,000/yr.

(F) **Effluent and Emissions - Treatment**

(a) Based on independent cost data, the treatment cost (primary and secondary only) amounts to approximately $7/Ton (Including power, oil, gas, labor, steam, air, chemicals, lime, phosphate, ammonia, sulfuric, special reagents).

(b) Selective reuse is made of separated and steam -(high percentage) stripped contaminated condensates within the mill. Cost incurred amounts to $1.90/Ton. Annual cost = 1.90 x 310,500 = $590,000/yr

(c) Annual savings is the differential for these treatments; namely, 310,500 ($7- $1.90) = $1,584,000

(G) **Water Consumption**

"Average" water quantity = 35,000 gpt (total)

"New" water quantity = 4,000 gpt (bleachery countercurrent use, etc.,)

= 20,000 gpt * (surface condensers, utilities, cooling)

*Thermally enriched water which can be discharged directly through the sewers or to the river or lake without effluent treatment. It may be reused in some locations (northern climates) or for associated mills. At millsites where temperature levels are of concern, cooling towers (as are now in use) are installed.

Overall decrease in water requirements = 35,000 - 24,000 = 11,000 gpt

$$\text{Savings} = \frac{11,000}{1,000} \times \frac{2}{100} \times 310,500 = \$68,000$$

Total Annual Savings = $5,363,000/yr.

**(i) The estimated amounts of the major savings (accounting for the "extra" steam consumed for the evaporation-crystallization phases of the SRP flowsheet) are tabulated herein based on various cost assumptions (listed for reference) which are considered quite conservative as compared to actual forecast or even present values.

(ii) If the conventional sequence $C\text{-}E_1\text{-}D_1\text{-}E_2\text{-}D_2$ is practiced and there is no reclamation of bleachery filtrate back through the unbleached pulp washing, there is no need "within" the mill to add extra balancing caustic (it would then dictate, however, installation and operation of external effluent treatment and use of additional lime to adjust effluent pH). Then the bleachery chemical cost would be $23.00/Ton.

NOTE: You may wish to consider partial recovery of effluent in some instances with evaporation of commensurate volume of white liquor to control the salt load.

(iii) No credit has been taken for the salt (NaCl) removed and purified in the SRP flowsheet. Average salt (basic price) cost is approximately 0.64¢/lb. Said sodium chloride may be reused for generation of bleachery agents—for roads or otherwise disposed of. If consumed, the savings = $120 \times 310,500 \times \frac{0.6}{100} = \$224,000$

(iv) No credit has been taken for the("low level") large heat quantity available from the thermally enriched water which may be of considerable economic use by associated facilities (surface condenser waters, etc.).

The term SRP as used in this comparison is a trademark of Erco Envirotech Ltd.

Biological Waste Water Treatment in the Presence of Steroid Compounds

S.V. Yakolev
T.A. Karjukhina

The principle possibility of stimulating the process of biological oxidation in aerobic conditions by means of addition of steroid compounds to the water to be treated was investigated.

As a basis for carrying out investigations, a known fact was taken which established experimentally that steroid compounds added to the culture medium have various effects on pure cultures of microorganisms.

Effects of three major types have been defined: steroids are growth factors; they would stimulate or inhibit metabolic processes in the cell; and would protect microorganisms against the action of toxic substances.

It is supposed, that some of the steroids would be toxic to the cell, and therefore, the transformation of steroids inside the cell, leading to formation of non-toxic substances, is a sort of protection of the microorganism. The action of four steroid hormonal preparations, produced on commercial scale, was investigated.

These are: methyltestosterone (I), testosteronepropionate (II), progesterone (III), pregnine (IV).

The first part of the investigations has been carried out using synthetic waste water (SWW), which included such components as peptone, buffer ammonium salts and dipotassium hydrogen phosphate (K_2HPO_4).

The first part of the investigations consists of three sets of experiments:

1. Oxidation in Warburg apparatus;
2. SWW treatment in mixing aeration tank models;
3. Aerobic mineralization of activated sludge (in models).

The conditions for carrying out the experiments and the results, which have been obtained for the sets of experiments, are briefly described below.

1. Oxidation in Warburg Apparatus.

Conditions of experiments:

—temperature of mixture - 25°C,

—concentration of activated sludge, adapted to SWW and to the appropriate steroid, is about 1 g/l,

—incubation time - 5 hours, reachings taken every half an hour.

The investigated substances are insoluble in water, therefore they were added to SWW in the form of alcoholic solution. The same amount of alcohol, but without any steroid, was added to the control flask.

The results of the first sets, averaged from many tests are shown in Table I.

Table I. Oxygen demand for 5h incubation % mg/l

Steroid	Steroid Concentration								
	0	1	2	5	10	15	20	25	30
I	100	141	115	105	113	89	92	-	44
II	100	161	142	136	112	116	116	100	103
III	100	127	113	107	104	103	100	104	99
IV	100	144	139	95	46	60	63	66	67

Note: Oxygen demand in the control flasks, taken as 100%, for experiments with substance I was 137 mg/l substance II - 249 mg/l, substance III - 176 mg/l and substance IV - 158 mg/l.

Conclusions:

a) Addition of steroids has a marked effect on the activated sludge oxygen demand in the process of peptone oxidation.

b) The action of the four compounds is of similar nature, while the degree of influence is different. Maximum increase in oxygen demand was observed at steroid concentration of 1 mg/l. Further increase in steroid concentration resulted in decrease of oxygen demand. Within the concentrations investigated two substances, I and IV, had an inhibitory effect, this being expected for substances II and III at concentrations above 20 mg/l.

c) Results of this set of experiments have confirmed, that it would be advisable to carry out investigations in aeration tank models with continuous cultivating of microorganisms.

2. SWW Treatment in Mixing Aeration Tank Models.

Experiment conditions: capacity of aeration tank model - 10 l, settling tank - from 1.5 l to 2.0 l. Time of each cycle - not less than 20 days (to obtain stable results) and not more, than 43 days. 5 cycles in total have been studied with aeration duration 12, 9, 6, 3 and 2 hours.

Table 2 shows basic results, averaged from 5 to 10 tests.

Discussion of the results obtained: The fact that BOD_5 of SWW with the steroid added is higher, than BOD_5 of the control sample is of interest. Increase in BOD_5 for the four preparations is different. The average increase in BOD_5 with the addition of substance I is 8%, substance II - 15%, substance III - 40% and substance IV - 68%. In three of the five cycles with aeration duration of 12, 9 and 6 hours tertiary treatment took place in all models. BOD_5 removal was actually the same for all aeration tanks, variations in effluent BOD_5 value being relatively small. Differences in effluent COD were observed, the COD of the water from the experimental models being somewhat lower, than that from the control models.

In 3 and 2 h cycles the treatment was incomplete. According to average results effluent BOD_5 was more, than 25 mg/l, and for individual samples up to 150 mg/l. Supposedly, there was no time for pregnine (IV) to be metabolized during such a short period of treatment, as effluent BOD_5 was higher than COD value.

Because of high sludge loadings, deficiency of dissolved oxygen was felt in some cycles that would partly limit the oxydation rates. The sludge of the first three cycles was swelled and rich in various Protozoa. In two last cycles the sludge index was very high. The sludge biocenasis of these cycles was noticeably poorer than in the first three sets.

Estimates of the amount of sludge growth have shown that under conditions of tertiary water treatment (in 12 and 9 h cycles) the growth in experimental aeration tanks was higher than in the control one, in 6 h cycle-approximately the same, and in 3 and 2 cycles lower than in the control unit.

As a result of comparison of relative effluent BOD_5 values and oxidation rates, it is possible to state that the presence of steroids makes the treatment of water more rapid and more effective. The latter is fixed by lower values of effluent COD in the experimental models (in the first three cycles); this means that substances, which are difficult to oxidize, have been implicated in the treatment processes.

Conclusions

a) The stimulating action of the steroids on the oxidation

Table 2. Performance of aeration tank model with the steroid substance added to waste water at concentration of 1 mg/l

Nos	Parameter	Aeration duration (h)																							
		12					9					6					3					2				
		Control	Aeration tank with substance				Control	Aeration tank with substance				Control	Aeration tank with substance				Control	Aeration tank with substance				Control	Aeration tank with substance			
			I	II	III	IV		I	II	III	IV		I	II	III	IV		I	II	III	IV		I	II	III	IV
1	Influent BOD_5 (mg/l)	555	580	632	740	900	583	608	6.58	663	918	563	660	650	745	954	516	590	634	798	837	527	607	648	1003	11
2	Effluent BOD_5 (mg/l)	12	13	9	16	17	17	17	18	18	23	16	14	5	20	12	25	19	30	30	140	22	39	47	38	1.0
3	Effluent COD (mg/l)	70	39	46	45	54	44	28	33	32	39	36	25	27	26	27	61	40	56	34	107	72	120	73	64	1.0
4	Sludge dosage (g/l)	2.5	1.9	1.8	2.6	2.6	2.5	2.1	2.4	2.3	2.2	2.4	2.0	2.1	2.4	2.2	2.6	2.1	2.5	1.9	1.9	2.7	2.8	3.1	2.8	1.0
5	O_2(mg/l)	2.5	2.9	3.0	1.7	1.0	1.4	2.0	3.2	1.3	1.3	1.2	1.6	2.3	1.7	0.8	0.7	1.0	0.9	0.5	0.7	1.1	1.0	0.9	0.7	1.0
6	Sludge index (mg/g)	303	298	-	375	360	375	-	354	328	349	70	351	389	360	312	431	437	408	420	427	344	251	311	369	29
7	BOD_5 oxidation rate (mg/g VSS per 1 hour)	26	34	41	33	40	35	42	42	43	63	51	72	71	68	94	83	120	111	178	159	137	138	130	222	383

processes have been observed in activated sludge during synthetic waste water treatment, prepared on the basis of peptone at steroid concentration of the treated water 1 mg/l.

b) Biological treatment of water will be more rapid and more effective in the presence of steroids. Substances, almost not available for activated sludge microorganisms under normal conditions, will be implicated in the oxidation processes.

c) The effect of the four substances studied was not specific; that allowed to considerable extend the sphere of search for most effective stimulators among the lots of steroid compounds.

3. Aerobic Mineralization of Activated Sludge.

Experiment conditions: capacity of mineralizer - 5 l. Steroid concentration in each model 0.2 mg/l. Experimet duration - 20 to 26 days. Activated sludge, adapted to the appropriate steroid (as from aeration tank models), was investigated, as well unadapted sludge, which was taken from the operating treatment plants of the city of Moscow. Temperature is 20°C.

The degree of activated sludge mineralization was estimated only as ash content.

Conclusions

a) Addition of steroids at concentration of 0.2 mg/l will stimulate processes of aerobic mineralization of sludge.

b) The effect of steroids will show in two ways and will result in reaching the required degree of mineralization for a shorter period of time or will ensure a higher degree of mineralization for the same time of treatment.

c) The effect of the steroids is not specific. Only the degree of influence of the steroid will be different.

The second part of the investigations has been carried out on municipal sewage, fed to the operating treatment plant of the city of Moscow. The second part consists of some sets of experiments for BOD_5 measurement by the dilution method.

The following problems have been investigated:

1) Effect of steroids on BOD_5 value of the clarified water, supplied to the biological treatment plant;

2) Effect of steroids on BOD_5 value of the effluent water from the aeration tanks of the plant.

3) Action of steroids, when an inhibitor of the biological treatment process, such as cuprous sulphate, was added to the waste water.

Some of the results obtained are described below.

1) Effect of steroids on BOD_5 of clarified water

Experiment conditions: steroid in the form of alcoholic solution was added to the diluting water, used for BOD measurement by the dilution method. The same quantity of the alcoholic solution was added to the control bottle, but without any steroid.

Results obtained and conclusions: some hundred of individual measurements have been carried out, both on single waste water samples and daily average ones. The addition of steroid varied within 0.1 mg/l and 2.0 mg/l. Substances I, III and IV were investigated.

The addition of alcohol resulted in sharp rise of BOD_5 value. During the investigations BOD_5 of the clarified water varied within 70 mg/l and 140 mg/l.

According to the quantity of alcohol added, BOD_5 of the control sample increased up to 202 mg/l to 1780 mg/l. This being so, it was found possible to show the effect of steroids only after a great number of experiments. Table 3 shows, as an example, the results obtained with progesterone (III).

Table 3

Concentration of substance III(mg/l)	BOD_5 of waste water (mg/l)		
	initial	with alcohol	with alcohol and III
1	2	3	4
0.1	100	202	208
0.2	97	308	320
0.3	104	429	437
0.4	95	528	561
0.5	137	712	671
0.6	139	745	799
0.7	93	997	948
0.8	71	872	992
0.9	110	1265	1225
1.1	96	1405	1360
1.3	122	1540	1350
1.5	86	1170	1118
1.7	88	1460	1288
1.9	92	1780	1620

Similar results have been obtained with other substances. Data in Table 3 show, that at progesterone concentrations of 0.1 mg/l to 0.8 mg/l, a small increase in oxygen demand will occur, while at concentrations above 0.8 mg/l there will be a decrease in oxygen demand, as compared with the control. Since in reality the addition of steroids in the form of alcoholic solutions is not advisable, subsequent experiments were carried out with the addition of investigated substances in the form of dry powders.

This version of the experiment gave a pronounced increase in BOD_5, and for progesterone, for example, the value was quite impressive - from 69% to 279% (see Table 7).

Conclusions

a) Addition of steroids will have a marked effect on BOD_5 value of the waste water, measured by the dilution method

b) The action of steroids will depend on the concentration of steroids.

c) Direct addition of the steroids in the form of dry powder will result in sharp stimulating of biological oxidation processes, when the dilution method is used for BOD measurement.

2) Effect of steroids on BOD_5 value of effluent water from the aeration tanks of the plant

Experiment conditions: steroids were added in the form of alcoholic solutions and dry powders.

The results, averaged from many tests, are shown in Tables 4, 5 and 6.

Table 4

Concentration of substance III (mg/l)	Effluent BOD_5(mg/l)		
	initial	with alcohol	with alcohol and III
0.2	9.6	202	181
0.3	8.1	241	301
0.5	6.5	509	520
0.7	6.5	635	621

Table 5

Concentration of substance (mg/l)	Effluent BOD_5(mg/l)	
	initial	with powder
0.1	10.5	12.4
0.2	12.0	13.0
0.3	10.9	12.0
0.4	9.9	13.5
0.5	10.9	11.5
0.6	10.9	13.6
0.7	11.4	13.4
0.8	13.8	15.6

Table 6

Concentration of substance III (mg/l)	Effluent BOD_5(mg/l)	
	initial	with powder III
0.5 - 2.0	3.5 - 16.4$^{x)}$ 9$^{xx)}$	20.0 - 78.1$^{x)}$ 57$^{xx)}$

Note: $^{x)}$ Variation limits
$^{xx)}$ Average BOD_5 value

Conclusions

a) Steroids will have a much more pronounced effect when added in the form of powder.

b) The degree of influence of various steroids will be noticeably different.

3) Effect of steroids with addition of inhibitor to waste water

Experiment conditions: Progesterone (III) was added to the clarified water in the form of dry powder. Cuprous sulphate and cuprous sulfate with progesterone were added to the parallel samples.

The results of the experiment are shown in Table 7.

Table 7

BOD_5 of clarified waste water (mg/l)			
Initial	with powder	with cuprous sulfate	with cuprous sulfate and II
108	208	65	105
110	186	75	118
76	288	34	206
62	215	87	184
76	208	53	132

Conclusions

a) Steroids would be used as measure for protection of activated sludge microorganisms against the action of toxic substances.

Some of the results, obtained for the effect of steroids on waste water treatment processes, briefly described here, allow to make the following general conclusions:

1. The group of steroid hormones is biologically active and will stimulate (or inhibit) treatment processes with complex activated sludge biocenosis.

2. Steroid substances will stimulate processes at low concentrations (up to 1 mg/l) and will inhibit them at high concentrations. Stimulation will manifest itself in implicating in processes organic substances, both exogenous and endogenous, which are difficult to oxidize and also in accelerating the processes.

3. The effect of the steroid hormones studied was not specific, while the degree of influence on the process was different, which will allow to extend the sphere of search for the most available, inexpensive and effective preparations.

4. In the processes of biological treatment of waste water in aeration tanks, many organic substances remain in the effluent water which would be oxidized if steroid stimulators were added to the water.

5. Investigations of technological aspects of the effect of steroid stimulators should be supplemented with biochemical investigations to elucidate the mechanism of action of the substances.

A Comparison of Conventional Activated Sludge Process and Pure Oxygen Activated Sludge Process for a 75-MGD Secondary Treatment Facility

Fred A. Harper,
General Manager
Orange County Sanitation Districts
California

This paper will discuss the process by which a pure oxygen system was selected over a conventional air system for a 75 mgd facility to adequately and economically produce the required effluent to meet State and Federal discharge requirements. Included in this discussion is a description of a pure oxygen wastewater treatment system for open tanks.

The Orange County Sanitation Districts provide for the collection,treatment and disposal of domestic and industrial liquid wastes for a service area of 320 square miles in Southern California, on the West Coast of the United States. The area has a population of 1½ million people in 23 communities, including the internationally known tourist attraction, Disneyland.

The agency operates two primary treatment facilities which are presently being upgraded to comply with State and Federal secondary treatment requirements. At Plant No. 1, which is a 50 million gallons per day (mgd) facility, an air activated sludge process plant is being constructed and is scheduled to be operational in January, 1977. Plant No. 2 is essentially a primary treatment facility, having a present rated capacity of 130 mgd average flow with a hydraulic maximum of 230 mgd.

Existing treatment comprises screening, pumping, grit removal, primary sedimentation, and chlorination when necessary. The effluent is pumped into the ocean five miles offshore through an outfall diffusion system some 6000 feet long. Sludge collected in the primary sedimentation basins is anaerobically digested and then dewatered by centrifugation. The dewatered sludge is sold to a soil supplement manufacturer.

A 1974 report investigated alternative wastewater treatment and disposal projects for meeting the State and Federal secondary treatment water quality goals and included the analysis for 16 candidate systems and an implementation schedule for improved treatment. This program called for staged additions totaling 175 mgd of secondary treatment at Plant No. 2. The first stage is a 75 mgd addition.

Four alternative systems were selected for final evaluation from the 16 candidate systems:

A. Air activated sludge
B. Pure oxygen activated sludge
C. Roughing filter and activated sludge
D. Roughing filter and pure oxygen activated sludge

The following preliminary design criteria and physical characteristics for the four alternatives for the 75 mgd facility were developed for the purpose of determining the necessary land requirements, energy demand, sludge production and over-all costs.

Primary effluent BOD_5 is assumed to be 225 mg/l, suspended solids 142 mg/l and grease 35 mg/l.

Aeration and oxidation facilities are sized based on a sustained 10-hour daily flow of 1.2 times the average flow. A sustained (peak month) primary effluent BOD_5 of 1.25 times the annual average BOD_5 and a sustained daily primary effluent BOD_5 of 1.20 times the daily average BOD_5 are also used as a basis for biological facility design. The over-all removal is assumed to meet the Federal effluent standards as follows:

BOD = 30 mg/l -Monthly Average
SS = 30 mg/l -Monthly Average

The wastewater flows entering the existing treatment facilities have shown peaks of nearly two times the average flow. These peaks lasted 8-10 hours and occurred when influent flow was actually restricted because of surcharged influent sewer lines. These conditions necessitate a peak design flow two times the average flow.

The following is a general comparison of normal operating and design parameters for pure oxygen and air activated sludge processes:

Normal operating and design parameters based on typical municipal sewage

Conventional Air Activated Sludge	Parameter	Pure Oxygen
3-8	Oxygenation Detention Time, Hrs.	1.0-2.5
2500-4000	Mixed Liquor Suspended Solids (MLSS), MG/L	3000-7000
2000-3200	Mixed Liquor Volatile Suspended Solids (MLVSS), MG/L	2500-6000
0.5-2	Mixed Liquor D.O., MG/L	2-6
30-75	Organic Loading, #BOD/1000 CF	100-250
0.15-0.40	Food to Mass Ratio (F/M), #BOD/#MLVSS	0.4-1.0
5000-15000	Return Sludge Concentration, MG/L	10000-30000
50-125	Return Sludge Rate, %Q	30-50
75-150	Sludge Volume Index, SVI	50-100
1.1-1.5	Oxygen Requirements, $\#O_2/\#BOD_5$	0.9-1.3
4-10	Oxygen Utilization, $\%O_2$ Supplied	85-90

Alternative A—Air activated sludge physical characteristics

Item	Design Value
Secondary Lift Station	
Aeration Basin Pumps	
Horsepower installed	1,200
Horsepower utilized	350
Blowers	
Aeration mode	diffused air
Air requirements, cfm (average)	142,000
Horsepower installed	9,200
Horsepower utilized	5,600
Aeration Basins	
Basin type	rectangular
Number basins	13
Length, feet	355
Width, feet	50
Sidewater depth, feet	15
Volume each, MG	2
Total volume, MG	26
Detention time, hours	8.3
Secondary clarifiers	
Basin type	rectangular
Number basins	22
Length, feet	150
Width, feet	40
Sidewater depth, feet	10
Surface area, each, ft^2	6,000
Waste activated sludge flotation thickeners	
Basin Type	circular
Number basins	4
Diameter, feet	40

Roughing Filter Concept

Use of roughing filters in a two-stage biological treatment scheme in conjunction with the activated sludge process has been found to have the following advantages: Reduction in applied aerator biochemical oxygen demand and consequent reduction in aerator volume; biological buffer for the activated sludge and subsequent prevention of aeration basin upset due to toxic loads; reduction in sludge volume; dampening of diurnal biochemical oxygen demand variation on the aeration basin; and the imparting of dissolved oxygen to the waste prior to aeration.

The literature contains numerous articles regarding plastic media filters and the roughing filter concept. Manufacturers have published data and extensive literature on the plastic media roughing filter. These data predict biochemical oxygen demand removals as high as 60 percent. Operating experience at other locales, though limited, verifies the roughing filter and air activated sludge process designs.

Effective five-day BOD removal is estimated to be 40 percent. If roughing filters are used in conjunction with intermediate clarifiers, it is estimated that BOD removals would be from 50 to 55 percent. Due to possible operational problems with pure oxygen and filamentous organisms, the roughing filter/pure oxygen activated alternative is analyzed herein with intermediate clarifiers. The conventional aeration alternative with roughing filters does not incorporate intermediate clarifiers.

The following illustrates the physical characteristics utilizing roughing filters for both the air activated sludge and pure oxygen activated sludge systems.

Alternative B—Pure oxygen activated sludge physical characteristics

Item	Design Value
Secondary lift station	
Aeration Basin Pumps	
Horsepower installed	1,200
Horsepower utilized	350
Oxygen generation and storage	
Oxygen absorption efficiency, percent	85-90
Installed oxygen supply, tons per day	150
Oxygen demand, average daily flow and average month BOD5, tons per day	91
Oxygen demand, average daily flow and maximum month BOD5, tons per day	110
Oxygen standby storage, tons	480
Horsepower installed	6,000
Horsepower utilized	2,000
Oxygenation tanks	
Mode	surface aeration
Basin type	rectangular
Sidewater depth, feet	17
Total volume, MG	8.4
Detention time, hours	2.7
Horsepower installed	2,400
Horsepower utilized	2,000
Secondary clarifiers	
Basin type	rectangular
Number basins	22
Length, feet	150
Width, feet	40
Sidewater depth, feet	12-14
Surface area, each, ft^2	6,000
Waste activated sludge flotation thickeners	
Basin Type	circular
Number basins	4
Diameter, feet	40

Air Activated Sludge

The air activated sludge process is well known and therefore will not be discussed in any detail. The costs associated with the enumerated physical characteristics for the air activated sludge facility include provisions for plug flow, step feed, and complete mix. In addition, costs for covering the aeration basins and scrubbing the foul air for odor control are included.

Pure Oxygen Wastewater Treatment in Closed Tanks

The use of pure oxygen in waste treatment is becoming popular in the United States and many installations are being constructed utilizing pure oxygen in closed tanks. The process is commonly known as the Unox System, developed by the Union Carbide Company.

This alternate system involves the production of oxygen gas followed by oxygen dissolution in closed tanks generally constructed with substantial freeboard. Oxygen dissolution in the mixed liquor will be accomplished by the use of high speed surface aerators in the closed tanks which achieve 85-90 percent utilization of the oxygen. The ability of the oxygen to be dissolved in the mixed liquor efficiently reduces the oxygenation detention time considerably over a conventional air activated sludge plant. This allows for oxygenation tanks to be smaller in size or greater flows can be treated in the same volume of tanks. The pure oxygen systems handle higher shock loads with less effect on the mixed liquor basin and over-all plant. This occurs because of the higher dissolved oxygen level which is maintained in the tanks.

Alternative C—Roughing filter and air activated sludge physical characteristics

Item	Design Value
Secondary lift station	
Roughing Filter Pumps	
Horsepower installed	1,660
Horsepower utilized	1,000
Aeration Basin Pumps	
Horsepower installed	1,200
Horsepower utilized	350
Roughing filters	
Basin type	circular
Number basins	2
Diameter, feet	145
Media depth, feet	20
Total volume, ft^3	660,000
Blowers	
Aeration mode	diffused air
Air requirements, cfm (average)	80,000
Horsepower installed	5,200
Horsepower utilized	3,100
Aeration tanks	
Basin type	rectangular
Number basins	9
Length, feet	355
Width, feet	50
Sidewater depth, feet	15
Volume, each, MG	2
Total volume MG	18
Detention time, hours	5.8
Secondary clarifiers	
Basin type	rectangular
Number basins	22
Length, feet	150
Width, feet	40
Sidewater depth, feet	10
Surface area, each, ft^3	6,000
Waste activated sludge flotation thickeners	
Basin type	circular
Number basins	4
Diameter, feet	40

Alternative D—Roughing filter and pure oxygen activated sludge physical characteristics

Item	Design Value
Secondary life station	
Roughing Filter Pumps	
Horsepower installed	1,660
Horsepower utilized	1,000
Aeration Basin Pumps	
Horsepower installed	1,200
Horsepower utilized	350
Roughing filters	
Basin type	Circular
Number basins	2
Diameter, feet	145
Media depth, feet	20
Total volume, ft^3	660,000
Roughing filter clarifiers	
Basin type	Rectangular
Number basins	16
Length, feet	150
Width, feet	40
Sidewater depth, feet	10
Surface area, each, ft^2	6,000
Flow capacity, each, MGD	4.7
Oxygen generation and storage	
Oxygen absorption efficiency, percent	85-90
Installed oxygen supply, tons per day	75
Oxygen demand, average daily flow and average month BOD$_5$, tons per day	60
Oxygen demand, average daily flow and maximum month BOD$_5$, tons per day	75
Oxygen standby storage, tons	240
Horsepower, installed	3,000
Horsepower, utilized	1,000

Alternative D—Roughing filter and pure oxygen activated sludge physical characteristics (continued)

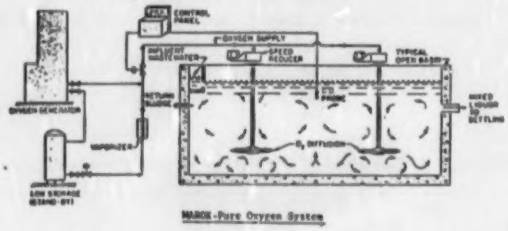
Item	Design Value
Oxygenation tanks	
Mode	Surface aeration
Basin type	Rectangular
Sidewater depth, feet	17
Total volume, MG	4.3
Detention time, hours	1.4
Horsepower, installed	1,200
Horsepower, utilized	1,000
Secondary clarifiers	
Basin type	Rectangular
Number basins	22
Length, feet	150
Width, feet	40
Sidewater depth, feet	12-14
Surface area, each, ft^2	6,000
Flow capacity, each, MGD	3.4
Waste activated sludge flotation thickeners	
Basin type	Circular
Number basins	4
Diameter, feet	40

Rotating Active Diffusers (RAD)

Each diffuser unit is a 7½ hp motor driven disc-shaped diffusion device having a porous ceramic medium installed in the anular space near the disc edge. As the RAD rotates at a constant speed of 76-82 rpm in the mixed liquor approximately 2 feet off the tank floor, the hydraulic sheer reduces the gas bubbles being diffused by the porous medium to 50 microns. Oxygen gas is transmitted through the hollow drive shaft to the diffuser disc at the bottom, then radially outward to the diffuser medium.

The typical process schematic shows the mixing action of the diffusers which are rated at 1500# O_2 per day with a 90% transfer to the mixed liquor. The tank mixing is achieved by curved radial vanes on the top and bottom surfaces of the diffusers. This action prevents the settling of the solids on the tank bottom and provides adequate contact between the mixed liquor and the diffused oxygen. The unique design of the disc prevents any buildup of scum or grease on the diffuser. A disc unit was removed after 7 months of continuous operation and flow tests determined that no plugging of the medium had occurred; there was only a slight discoloration to the ceramic medium.

Pure oxygen wastewater treatment in open tanks


CONTROL PANEL
OXYGEN SUPPLY
SPEED REDUCER
TYPICAL OPEN BASIN
OXYGEN GENERATOR
D.O. PROBE
MIXED LIQUOR TO SETTLING
VAPORIZER
O_2 DIFFUSION
MAROX-Pure Oxygen System

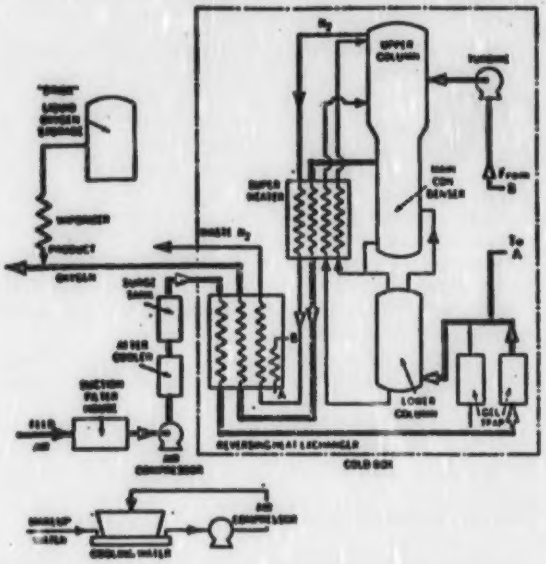
MAROX-Pure Oxygen System
Typical process schematic

This method, utilizing fine bubble diffusion, is capable of reacting extremely fast to changes in demand as oxygen, instantaneously sensed and indicated through the use of dissolved oxygen probes and analyzers, is fed directly into the diffuser and then directly into the mixed liquor. The time elapsed from a change in oxygen demand in the tank until a change in oxygen diffused by the dissolution equipment is only a matter of seconds.

Operational Performance

Typical performance of the MAROX System applied to municipal wastes is shown in the accompanying data.* The municipal plant data was observed in full-scale pilot and demonstration plants treating primarily domestic waste during 1973 through 1975. (*Supplied by MAROX manufacturer.)

	Installations			
	A	B	C	D
Detention Time, Hours	1.1	2.0	1.9	2.3
Biomass Loading, F/M, lb BOD_5/day/lb MLVSS	1.02	0.71	0.56	0.59
Organic Loading, lb BOD_5/day/1,000 cf	244	133	141	110
Mixed Liquor TSS, mg/l	4,743	3,730	4,859	3,846
Mixed Liquor VSS, mg/l	3,886	3,060	4,217	3,110
Recycle TSS RAS, mg/l	12,221	11,390	13,461	9,870
Water Temperature, °C	19.0	15.6	15.7	16.0
SVI	67.8	79	78	84
SRT, days	6.2	3.5	7.5	6.8
Clarifier Overflow, GPDPSF	617	577	614	523
Oxygen Usage, lbs O_2 supp/lb BOD_r	0.92	1.12	1.11	1.37


N_2
UPPER COLUMN
TURBINE
LIQUID OXYGEN STORAGE
VAPORIZER
PRODUCT
OXYGEN
SUPER HEATER
MAIN CONDENSER
From B
To A
WASTE N_2
SURGE TANK
AFTER COOLER
SUCTION FILTER HOUSE
FEED AIR
AIR COMPRESSOR
LOWER COLUMN
GEL TRAP
REVERSING HEAT EXCHANGER
COLD BOX
COOLING WATER

Schematic flow diagram cryogenic oxygen plant plant no. 2

Pure oxygen waste treatment in enclosed tanks

Pure Oxygen Wastewater Treatment in Open Tanks

While most pure oxygen wastewater treatment installations currently being constructed utilize the closed tank concept, another pure oxygen dissolution technique has been evolving in the United States. It is a diffuser system which generates very fine pure oxygen bubbles deep in the mixed liquor, achieving 90% or greater oxygen transfer. The process, known as the MAROX System, has been developed by the FMC Company of Chicago, Illinois.

Covered tanks are not needed because of the efficient transfer of oxygen in the mixed liquor and since there is little surface agitation, no more than two feet of freeboard is necessary.

MAROX System

The system is comprised of three major components:

1. A source of pure oxygen gas such as on-site cryogenic oxygen supply system. The cryogenic process has been in wide use for many years in the United States with

thousands of existing industrial installations.

2. An oxygen dissolution system utilizing "Rotating Active Diffusers" (RAD). Pure oxygen gas, in the form of minute (50 micron) bubbles, is simultaneously introduced deep into mixed liquor via RAD to accomplish the mass oxygen transfer.
3. The system is controlled by an automatic dissolved oxygen control system that accurately monitors and controls the DO level. DO sensors are strategically located in the mixed liquor to automatically regulate oxygen flow to the diffusers. Mixed liquor is constantly monitored and consistently maintained within 1.0 mg/l even through diurnal flow variations.

Upgrading Existing Air Diffuser Systems

The MAROX system is appropriate for upgrading treatment facilities. Most existing aeration tanks can be utilized by the addition of the diffuser equipment and a source of oxygen gas. With minimal modifications to the tanks, the capacity of the mixed liquor basins can be increased several fold. A recent conversion at a treatment facility in Colorado was completed in 6 weeks after fabrication of the diffusers. The tank was upgraded from a 3 mgd air diffuser system to a 10 mgd MAROX system.

Thirteen RAD diffusers replaced 21 air diffusers in a basin 210 feet long, 25 feet wide and 17 feet deep. Six RAD diffusers were paired at 21-foot intervals at the inlet end of the tank and monitored by a DO probe.

A second DO probe monitored the next four diffusers which were mounted singly at 21-foot intervals in the center of the basin.

A third probe monitored the remaining three diffusers which were spaced uniformly at the outlet end of the tank.

Observations of the MAROX System

1. The system appears to be very simple to operate since the oxygen feed rate to the diffuser system is automated to the dissolved oxygen of the mixed liquor.
2. Open tank construction with minimal freeboard means savings in capital construction costs compared to closed tank systems.
3. This system appears ideal [illegible] pre-aeration or pre-treatment modes because each diffuser unit is complete in itself, the spacing can be arranged to put the greatest oxygen supply in areas of greatest demand.
4. Existing aeration tanks can be upgraded with minimal modifications in a short period of time.
5. The danger of explosive mixtures associated with pure oxygen is minimized with the open tank system when compared to the closed tank system.

Conclusions

Land Requirements

Like many waste treatment facilities in highly urbanized areas, the agency's two treatment facilities, which comprise approximately 100 acres each, are surrounded by residential and industrial development. Because of this, it is important to conserve all usable land space when expanding for projected flows of 320 mgd in the year 2000, by employing processes which can concentrate treatment in compact facilities. In addition, we must provide odor abatement facilities and incorporate these features into new construction whenever possible. The pure oxygen activated sludge process utilizes the least amount of land.

Land requirements

Alternate	Acres	Acres for Structures
A	13.1	8.6
B	10.7	6.2
C	13.9	9.4
D	11.5	7.0

Secondary Sludge Generation

While it would appear that Alternate D generates the least amount of sludge, there is no difference between Alternates D and C, since the intermediate clarifier sludge returns as primary sludge. The difference in secondary sludge generation is not significant in the selection of the alternate process.

SECONDARY SLUDGE GENERATION - 75 MGD
(pounds dry solids per day)

	Secondary Sludge Generation		
Alternate	Raw (dry #/day)	Digested (dry #/day)	Digested* (cubic yards/day)
A	96,000	54,000	142
B	96,000	54,000	142
C	77,000	46,000	121
D	71,000	42,000	110

**Assumes 20% solids with 90% solids capture from centrifuges*

Energy Requirements

The projects analyzed require significant amounts of energy to operate; much of the energy will be available on site in the form of digester (methane gas from biological treatment alternatives.

In the analysis, equipment (installed) horsepower is estimated to exceed the horsepower utilized daily. This is normal practice to insure sufficient power and equipment in cases of equipment failure, maintenance work, and peak load periods. Much of the utilized horsepower needs may be met by use of digester gas for fueling engines, boilers, incinerators, and other equipment for the biological treatment alternatives. Not all equipment can be operated on this fuel, and alternative power sources are needed to ensure continuous, uninterrupted treatment and pumping processes during normal circumstances, during emergencies, and during natural disasters.

Energy requirements

Alternate	Installed Horsepower	Utilized Horsepower	Horsepower from Digester Gas	Purchased Horsepower
A	12,609	8,406	2,923	5,483
B	8,745	5,830	2,423	3,407
C	9,889	6,593	1,943	4,650
D	7,500	5,000	2,796	2,204

Cost Analysis

A detailed cost analysis was performed on each of the alternatives set forth herein. All costs are based on the same construction cost index. Capital costs were developed from the construction bid for the 50 mgd activated sludge plant currently under construction at Plant No. 1, from manufacturers' quotes, and from other similar construction jobs. The costs are estimated for a 75 mgd increment of secondary treatment. They include a secondary pump station, secondary treatment basins and clarifiers, roughing filter and aeration basin covering for odor control, air or oxygen supply facilities, sludge thickeners, yard work, instrumentation, construction of an electrical service entrance, and emergency power generation. Oxygen generation facilities considered are cryogenic units, which are more economical than other oxygen generating facilities for quantities necessary herein.

Capital Cost

The total project capital cost was determined by estimating the construction cost and then adding 43 percent to cover contingencies, engineering, legal and administrative costs, and interest during construction in conformance with Federal guidelines.

Definitions:

BOD_5—Biochemical oxygen demand - 5 day
SS—Suspended solids
F/M—Food to microorganisms
MG/L (mg/l)—Milligrams per liter
MLSS—Mixed liquor suspended solids
DO—Dissolved oxygen
MG—Million gallons
MGD (mgd)—Million gallons per day
ft^2—Square feet
ft^3—Cubic feet

Recommended Project

On the basis of the analysis presented, an evaluation of alternatives has shown the pure oxygen activated sludge process to be the most cost-effective for secondary treatment.

Pure oxygen activated sludge offers an 18 percent savings in project cost over the next cost-effective alternative. The recommended alternative provides a degree of treatment which will meet secondary treatment effluent quality limits and will provide a cost savings for maintenance, operation, and power over the conventional aeration secondary treatment alternatives. Digester gas generated from the 75 million gallons per day treatment scheme will provide 5,830 horsepower. This recommended alternative also provides a savings in land utilization over other alternatives.

The costs enumerated for the pure oxygen activated sludge process are based on the closed tank system. For construction competition purposes, relatively few additional drawings are needed when both the closed tank and open tank oxygen systems are under consideration. Only the oxygenation tanks and associated electrical requirements are different, while the oxygen gas production and the final clarification systems are similar. For example, only 8 additional design sheets were required to determine competitive costs recently for a proposed 20 mgd oxygen treatment facility.

Monetary cost of alternatives

		Alternate A Air Activated Sludge	**Alternate B** Oxygen Activated Sludge	**Alternate C** Roughing Filter and Air Activated Sludge	**Alternate D** Roughing Filter and Oxygen Activated Sludge
Construction cost		$49,705,000	42,193,000	49,682,000	51,369,000
Annual costs					
Capital Recovery	$/MG	233	203	233	244
Maintenance	$/MG	29	25	29	30
Operation	$/MG	9	9	10	10
Power	$/MG	43	24	33	23
Chemicals	$/MG	1	1	1	1
Interim Sludge Disposal	$/MG	34	34	32	32
Total annual cost	$/MG	349	296	338	340

Studies of Artificial Aeration in the Lithuanian SSR.

Skirckiavichus A.L.
The Kaunas Polytechnic
Institute of Snechkus A.

All our efforts to treat wastewaters result in pure water and rivers useful for beneficial purposes. Therefore further treatment of effluents discharged from treatment plants may be necessary. The effluent residual BOD presents considerable loading for receiving waters, especially if they are not large.

For example an average industrial town (on the Lithuanian SSR scale) produces 50,000 cu.m. of wastewaters having a BOD$_5$ 700 mg/l or 35 T. BOD$_5$ per day. This BOD value is typical for wastewaters discharged by our towns having food-processing industry. At 95 percent treatment efficiency residual BOD$_5$ will be 1,75 T. per day and equal to load produced by 32,000 inhabitants.

Attention should be given to river pollution caused by urban storm waters, drainage waters and effluents from small agricultural areas, where chemicals and fertilizers are widely used their load may be significant.

Biological treatment process also takes place in rivers where all these pollutants go into with natural waters or sewage and therefore it should be subjected to adequate control.

During the dry summer period at high temperatures or the winter period when ice cover inhibits natural surface aeration temporary bad river conditions may bring to naught all attempts and expenditures spent on wastewaters treatment.

Artificial aeration is a method which prevents anaerobic in the river and promotes destruction of contaminants. The studies of artificial aeration have been conducted by the Kaunas Polytechnic Institute and the Ministry of Municipal Economy since 1971.

The investigations were conducted at the Nevejis River polluted by insufficiently treated wastewaters of Panevejis-town. For these purposes the experimental unit "NEVEJIS-1" with mechanical C-16 type aerators developed by Vitols O. and Resinsh was established at the river. The capacity of an aerator is 2.2 kw. They were mounted from 4 to 9 in number on metal frame which was fixed to supporting pontoons. The river width in this region is 16-20 m, frame length is 12 m. So the cross-section of the river was wholly included into aeration zone.

The DO concentrations have been measured by electrochemical DO analyzer of UT-6803 type developed by Tartu State University.

Special studies were conducted to select DO sampling point at cross-sections, to determine reiteration of measurements and to choose upstream and downstream cross-sections for sampling.

Detailed measurements of DO were made in a number of cross-sections at 5-10 m. distance downstream and upstream from aerators when they were in operation and out of operation. Variation-static method was used to work up data and to estimate accuracy of measurements.

Downstream cross-section for sampling has been selected in such a way that the DO concentration variation coefficient didn't exceed the value of the coefficient for the same cross-section under natural conditions (aerators are turned off).

On the basis of analysis of static characteristics it has been found that samples to be taken at the depth of 0.3 m; reiteration of measurement should be more than 5; the duration of five time measurement shouldn't exceed 4-5 min., downstream sampling point should be at 50m. distance from an aerator. Upstream sampling point is assumed to be at the same distance from an aerator proceeding from convenience in sampling and calculations. Measurements were made at cross-sections taking into account the flow time between sampling points.

For comparison of results obtained from particular tests under different conditions data have been converted to standard conditions (river temperature is 20°C, 0 percent DO saturations, pure water, 760 mm Hg pressure).

If rotor is submerged at 1,0 m depth and aerators are mounted at 3m distance from each other average oxygenation capacity at standard conditions is 1,14 kgO_2/kwh. This value is lower than those obtained according to data which were reported by American (1,34 kgO_2/kwh) and German (1,37 kgO/kwh) investigators. It is evident that the difference is negligible. It can be attributed to low flow rate, as it has been found efficiency of artificial aeration increases with increasing flow rate.

In practice this efficiency was obtained during tests on turbine suction aerators having a capacity of 30kw.

DO saturation should be better under actual river conditions in comparison with that in tanks under steady-state conditions, due to a new dosage of water with high saturation deficit of DO which reaches aerator all the time. But oxygenation capacity of aerators of all types is lower than that achieved under non-flow conditions. Similar results have been reported by foreign scientists Huntre J.V. Whipple W. et al. Probably it may be explained by the fact that there is no standard method for evaluation of aerator's efficiency. Of course reasons will be further investigated, but at present while designing this fact should be considered and aerator efficiency index which is about 0,33-0,4 should be introduced into coefficient.

Studies of barbotage aeration also were conducted at the experimental unit. Aerators- plastic corrugate drainage pipes with a diameter of 50mm and a length of 2,20m- were put on branch pipes welded to a steel pipeline which was laid across the river. 1080 openings with a diameter of 1,5mm were made at each meter along aerator's length. Total openings area on one running meter of the pipe is 0,00191 sg.m. Air was provided by air blower approximately 60 cu.m. in hour per one aerator. Efficiency of oxygen consumption is 2.2 percent. Average air rate at outlets is 4m/sec. Oxygenation capacity of barbotage aeration at standard conditions is 0,99kg O_2/kwh or 13 percents lower than that of mechanical aeration.

Barbotage aeration has such shortcoming as the noise which is produced by air blowers. This disadvantage limits its application in densely populated areas of the Lithuanian SSR. The construction of special buildings for air blowers increases the construction cost of artificial aeration unit.

As a result of DO tests carried out at weirs it was concluded that weirs for artificial aeration should be constructed with a height of to 1,0 m. Weir should be with a free-spilling jet and reaches conjugated according to submerged hydraulic jump.

Studies of artificial aeration were conducted at PpK 70-BO-100 Kruosta hydraulic turbine. Air was supplied through pipes in upper cap of a turbine which connect zone of discharging with atmosphere.

In the course of aeration the DOconcentration varied in the range from 0,55 to 1,70 mg/l. The loss of a unit capacity was ranging from 4,8 to 8,7 percent during artificial aeration.

Average oxygenation capacity under standard conditions is 2,58kgO_2/kwh. The efficiency of artificial aeration by hydraulic turbine is higher than those obtained by other methods.

Investigations showed that above mentioned value of capacity loss was conventional. Discharge which doesn't pass through hydraulic turbine due to artificial aeration, remains in head race and naturally conserves its potential energy. So when not all of the turbines are in operation and there is no dummy discharge saved flow rate passes through another hydraulic turbine. Thus amount of energy generated by hydropower station as a whole decreases slightly. Only amortization of units increases due to their operation together for longer time than that without aeration. Therefore aeration efficiency of the hydropower station estimated by this method is up to 12,94kgO_2/kwh or 17,86 kgO_2/kwh under standard conditions.

The results of the studies conducted to determine the effect of artificial aeration on self-purification properties of the receiving waters didn't show improvement in self-purification properties. Variations in BOD and COD values were nearly the same during artificial aeration as well as without it and didn't indicate an obvious relationship.

The same results were achieved during microbiological tests. Only number of anaerobic bacteria decreased slightly. Index of testing on glander ranged equally with aerators in operation as well as out of operation: ranging from 2,6-3,0 in the region in front of aerators to 2,2-2,75 at the 5km potion behind cross-section of artificial aeration.

As a result of analysis of data taking account of literary data the following conclusion can be drawn: under aerobic conditions the increase in the DO concentration doesn't intensify self-purification process significantly.

It conforms to Phelpth-Striter theory. According to it the rate of BOD removal is directly proportional to BOD value and is independent of DO content in water. Of course it may exist until anaerobic conditions will occur which inhibit self-purification process. According to Velner CH A, Melder Ch.A. and Laene A.A. maximum rate of aeration is determined at DO concentration ranging from 1,5 to 2,5 mg/l. Probably the DO concentration shouldn't be less than above given values below the place of wastewater discharge under extreme conditions (low flow rate, high temperatures, ice cover etc.)

If anaerobic conditions exist in front of artificial aeration zone, aeration promotes self-purification process. Sometimes it requires a certain time depending on the degree of anaerobics in the region in front of the cross-section of reaeration. Of course during artificial aeration the process restores more rapidly than that under natural conditions.

The effect of artificial aeration on oxygen regime in the river is estimated by comparison of slopes of oxygen curves (mgO_2/l/km) prior to and after artificial aeration.

The definition "slope of oxygen curve" (mgO_2/l/km) in our view reflects fully the dissolved oxygen saturation process in conjunction with reaeration.

As a result of investigations it has been found that the slope of oxygen curve increases slightly (7-11%) if artificial aeration unit is located in the descending potion of oxygen curve. It may be attributed not to increase in the rate of self-purification process and oxygen consumption but to decrease in the rate of natural surface reaeration due to increased saturation of water with oxygen.

Artificial aeration is graphically shown in Figure 1 considering all above mentioned conclusions.

Prior to wastewater discharge to receiving waters (point 1) BOD value is normal and DO concentration is high and near saturation value. Pollutant concentration increases during wastewater discharge. Intensive self-purification process starts below the point of discharge. BOD concentration reduces and natural surface reaeration can't supply sufficient amount of oxygen. The oxygen curve descends rapidly and intersects line of desired minimum concentration (1,5-2.0 mgO/l) at point 2. Normal aeration process is broken, fish is killed, self-purification process is inhibited considerably.

At point 3— oxygen supply is exhausted, anaerobic digestion process occurs. BOD concentration doesn't reduce and even increases due to secondary pollution.

At a certain distance at point 4 air supply again exceeds oxygen consumption its concentration restores and reaches level of desired minimum concentration at point 5, above which self-purification process takes place under normal conditions. Thus under natural conditions normal process of self-purification doesn't occur in the river potion with L length, between points 2 and 5.

If artificial aeration is applied at point 2, DO concentration increases BOD removal goes on. If it is necessary artificial aeration is applied at several cross-sections (e.g. at point 3, 4) until oxygen curve reaches point 5. Self-purification process goes on all the time under normal aerobic conditions and ends somewhere at point 6, which is located nearer than that under the same conditions without artificial aeration.

Of course pollutants concentration exceeds normal value in the region between points 2 and 6, it isn't so dangerous due to presence of oxygen. If we must select either "dead stream" that is with zero. DO concentration of "alive river" although it doesn't meet water quality standards, the latter should be chosen. As we have already seen such alternative may arise with any small stream, even if we have good wastewater treatment plants.

Wastewater treatment plants can't be replaced by artificial aeration and therefore we shouldn't exaggerate its possibilities. However more attention should be paid to artificial aeration as an economical and effective method of a partial solution to river DO problems at present day growth of pollution.

The Kaunas Polytechnic Institute continues studies of artificial aeration. The design of powerful summer unit of artificial aeration has been performed and it should prevent formation of regions with anaerobic conditions in the Nevejis River until wastewaters discharged by Kedainiay town will receive sufficient treatment. Unit's capacity is 600kw. Oxygenation capacity is approximately 7000kg DO/day. At present the possibility of constructing the aeration unit in 1977 is being considered.

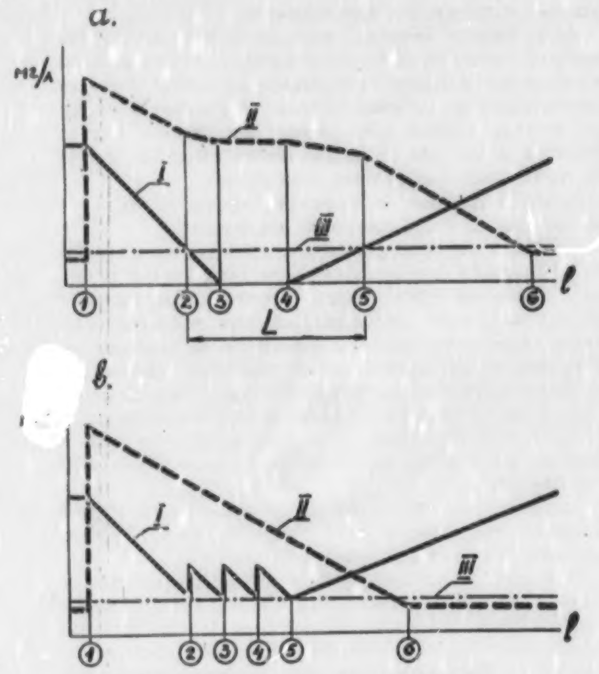


Fig. 1. Self-purification process in overloaded river.
a. River aeration;
b. Artificial aeration;
I. DO concentration;
II. BOD concentration;
III. Desired minimum DO concentration.

Wastewater Treatment Concerns of the Organic Chemicals Industry in the United States

Carl E. Adams, Jr., Ph.D., P.E.
President
Associated Water & Air
Resources Engineers, Inc.
Nashville, Tennessee

Billy T. Sumner, P.E.
Immediate Past President
American Consulting Engineers Council
Vice President
Barge, Waggoner, Sumner and Cannon
Nashville, Tennessee

July 1976

I. Introduction

The organic chemicals industry is the most complex and diversified industry in the United States. It not only generates thousands of different products, but even produces at different plants identical chemicals by different processes.

Synthetic organic chemicals are products derived from naturally-occurring raw materials—primarily from petroleum, natural gas, and coal—that have undergone at least one chemical conversion. Originally, coal was the primary raw material for the organic chemicals industry, but in the last 20 years, it has been replaced by petroleum-based feedstocks because, even though the price of coal is less than one-half that of most fluid feedstocks, the handling and processing of fluids is more economical. Moreover, the mining of coal is far more labor-intensive than the extraction of fluid fuels from the earth. The term "petrochemical" is commonly used to refer to all organic chemical products derived from petroleum fractions and by-products or from natural gas constituents.

Within the last 10 years, there has been an extraordinary simplification of numerous organic syntheses, chiefly because of unique developments in catalysis and automatic control. This, combined with the construction of larger and larger production facilities, has resulted in a drop in the price of organic chemicals that would not have been thought possible a few years ago.

This trend toward lowering production costs is counterbalanced by a rapidly developing crisis in the organic chemicals industry: the diminishing availability of economical raw materials. The chemical manufacturers are now paying more and more for crude oil and natural gas—a situation that is expected to become more severe. In addition to this economic problem, the industry is confronted with the cost of complying with the pollution abatement goals established by the federal government.

II. Categorization of the Organic Chemicals Industry

There has been an effort in the United States to establish effluent discharge limitations for each major industrial product. For some industries, such as pulp and paper, relatively broad effluent guidelines that apply to certain segments of these industries can be established. However, this is impossible for the organic chemicals industry in which increasingly complex technologies produce a diversity of interrelated chemicals by a variety of processes. The water usage and subsequent discharges of wastewater are directly related to this mixture of products and processes. Therefore, the federal government has prepared effluent limitations for the organic chemicals industry as a whole with subcategories that are related to the manufacturing process and the extent of water usage within the process. There are four major subcategories:

Subcategory A: Nonaqueous Processes

This subcategory is limited to processes in which there is minimal contact between water and the reactants or products; water is not required as a reactant or diluent and is not generated as a reaction product. The water usage in this category would result only from necessary washes or catalyst hydration.

Subcategory B: Process Water Contact as Steam Diluent or Adsorbent

This subcategory is limited to processes in which water is utilized in the form of dilution steam, direct product quench, or adsorbent for effluent gases in reactions that are all vapor-phase over a solid catalyst. Most processes in this subcategory utilize an adsorbent combined with steam stripping of chemicals for purification and recycling.

Subcategory C: Aqueous Liquid-Phase Reaction Systems

This subcategory includes processes in which the reactions are liquid-phase with the catalyst in an aqueous medium. Continuous regeneration of the catalyst requires extensive water usage and in some cases substantial removal of inorganic by-products. This subcategory also includes processes in which water is involved in the final purification or neutralization of products.

Subcategory D: Batch and Semicontinuous Processes

This subcategory includes the processes in which the reactions are liquid-phase with aqueous catalyst systems; in which very rapid cooling makes it necessary to add contact quench water or ice; or in which the reactants and products are transferred through the various processes by gravity flow, pumping, or pressurization. This subcategory also includes processes in which much of the materials handling is manual; in which solids-liquid separations are common and employ filter presses and centrifuges; or in which air or vacuum ovens are used for drying products: a major source of wastewater results from cleaning the noncontinuous production equipment.

All effluent limitations and treatment technologies for the organic chemicals industry were defined on the basis of these four subcategories. In addition, Subcategories B and C were further subdivided according to raw waste loads by groups—B-1, B-2, C-1, C-2, C-3 and C-4—that consist of product/process segments with similar raw waste load characteristics for the major pollutant parameter, biochemical oxygen demand (BOD).

III. WASTEWATER CHARACTERISTICS FOR THE ORGANIC CHEMICALS INDUSTRY

Because of the diversity of the organic chemicals manufacturing processes, practically every significant pollution parameter exists at one plant or another. Some waste streams may contain only two or three significant parameters, whereas others may contain as many as 50 or 60 significant constituents. After extensive literature review and numerous field surveys, the federal government concluded that there are only 27 that significantly affect the quality of surface waters (see Table 1). Of course, the effluent limitations include the usual pollution indicators: biochemicals oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), etc. In addition, there are other limitations that, for the most part, pertain to dissolved organic pollutants in process wastewater. No specific limitations were proposed for pollutants associated with non-contact wastewater like boiler and cooling-tower blowdown because these waste streams primarily contain inorganic materials and it is difficult to allocate such wastes to specific processes in multi-product plants.

Other parameters considered include total organic carbon, ammonia, cyanide, extractable oils and grease, and various heavy metals. These were generally found to be in concentrations substantially lower than those that would require specialized end-of-pipe treatment, i.e., treatment that is not an integral part of the industrial process.

Summaries of the amount of flow, BOD and COD for Subcategories A, B, and C are shown in Tables 2, 3, and 4, respectively. There is insufficient data at this time from Subcategory D processes; however, Table 5 does show some data from a batch organic chemical plant producing azo dyes.

Table 1
Significant pollutant parameters for the organic chemicals industry

General Parameters	Organic Pollutants and Nutrients
1. Biochemicals Oxygen Demand (BOD)	15. Totals Organic Carbon (TOC)
2. Chemical Oxygen Demand (COD)	16. Ammonia Nitrogen
3. Total Suspended (Nonfilterable) Solids (TSS)	17. Total Kjeldahl Nitrogen (TKN)
4. Total Dissolved (Filterable) Solids (TDS)	18. Phenols
5. pH	19. Cyanide - Total
6. Acidity	20. Phosphorus - Total
7. Alkalinity	**Metals**
8. Hardness - Total	21. Zinc-Total
9. Calcium - Total	22. Copper-Total
10. Magnesium - Total	23. Iron - Total
11. Chloride	24. Chromium - Total
12. Sulfate	25. Cadmium - Total
13. Color	26. Cobalt - Total
14. Oil and Grease	27. Lead - Total

Table 2
Summary of raw waste load data
Subcategory A - nonaqueous processes

Product/Process	**Flow**		**BOD**	**COD**
	liters/1000 kg	*gal/1000 lb*	*kg/1000 kg*	*(lb/1000 lb)*
BTX Aromatics (Hydrotreatment)	114.0	13.6	0.10	0.31
BTX Aromatics (Solvent Extractin)	504.0	60.4	-	-
Cyclohexane	No Discharge			
Vinyl Chloride	2,004.0	240	-	0.12
Mean Value	873.0	105.0	0.10	0.22

Table 3
Summary of raw waste load data by subcategory group
Subcategory B - processes with process water contact as steam diluent or adsorbent

B-1 Product/Process	**Flow**		**BOD**	**COD**
	liters/1000 kg	*gal/1000 lb*	*kg/1000 kg*	*(lb/1000 lb)*
Ethyl benzene	317	38	0.13	1.86
Ethylene and Propylene	2,961	355	0.35	2.36
Butadiene (from ethylene)	1,693	203	0.63	2.04
Methanol	417	50	0.49	0.94
Acetone	1,460	175	0.26	1.10
Vinyl Acetate	234	28	0.04	0.13
Formaldehyde	1,093	131	-	-
Ethylene Oxide	617	74	0.7	6.48
Ethylene Dichloride	800	96	-	4.84
Vinyl Chloride (from ethylene dichloride)	2,802	336	-	7.66
Methyl Amines	3,661	439	0.48	12.8
B-1 Mean Value	1,460	175	0.38	4.0
B-2 Product/Process				
Acetaldehyde (from ethanol)	13,344	1,600	1.12	2.48
Butadiene (from n - butane)	9,674	1,160	2.96	3.23
Acetylene	4,679	561	1.92	5.95
Styrene	14,453	1,733	1.00	3.74
B-2 Mean Value	10,541	1,264	1.75	3.85

Table 4
Summary of raw waste load data by subcategory group
Subcategory C - aqueous liquid phase reaction systems

C-1 Product/Process	**Flow** *liters/1000 kg*	*gal/1000 lb*	**BOD** *kg/1000 kg*	**COD** *(lb/1000 lb)*
Coal Tar (pitch forming	1,043	125	-	0.06
Acetic Acid	4,170	500	0.35	0.78
Acrylic Acid	3,962	475	0.74	1.64
Ethylene Glycol	4,871	584	0.34	8.76
Terephthalic Acid	1,551	186	0.82	1.72
C-1 Mean Value	3,119	374	0.56	2.59
C-2 Product/Process				
Acetaldehyde (ethylene and oxygen)	509	61	1.9	5.8
Phenol and Acetane (cumene process)*	2,335	280	5.6	11.0
OXO Chemicals	3,503	420	3.2	4.25
Coal Tar (distillation)	3,336	400	2.8	8.7
Caprolactam	10,842	1,300	1.6	4.0
C-2 Mean Value	4,103	492	3.03	6.75
C-3 Product/Process				
Acetaldehyde (ethylene and air)	751	90	26.6	44
Anilene	1,585	190	-	21.2
Bisphenol A*	559	67	-	17.1
Dimethyl Terephthalate	2,252	270	24.4	38.2
C-3 Mean Value	1,284	154	25.5	30.1
C-4 Product/Process				
Acrylates	23,819	2,856	47	118
P - Cresol*	10,767	1,291	123	256
Methyl Methacrylate	1,668	200	45	386
Terephthalic Acid (nitric acid process)	5,496	659	59	104
Tetraethyl Lead	100,000	12,000	-	110
C-4 Mean Value	28,366	3,401	68.5	195

**Phenols raw waste load - 10 kg/1000 kg (lb/1000 lb)*

Table 5
Summary of raw waste load data
Subcategory D—batch and semi-continuous processes

Product/Process	*liters/1000 kg*	**Flow** *gal/1000 lb*	**BOD**	**COD** *kg/1000 kg (lb/1000 lb)*	**TOC**
Azo Dye (Batch)					
@ 50% occurrence	793,826	(95,069)	79	1,850	790
	114,395	(13,700)	220	1,075	450
	175,768	(21,050)	59	175	60
Mean Value	361,329	(43,273)	119	1,033	433

IV. Wastewater Control and Treatment Technology

Three distinct levels of technology are being utilized to reduce the concentrations of various pollutants to the levels required by law and are defined as follows:

1. *Best Practical Control Technology Currently Available (BPCTCA),* which represents the quality that must be achieved no later than July 1, 1977.
2. *Best Available Technology Economically Achievable (BATEA),* which is more stringent than BPCTCA and will be required by July 1, 1977, in those situations in which water quality has deteriorated so much that improvements beyond BPCTCA are necessary. This technology will be required for *all* treatment facilities by 1983.
3. *Best Available Demonstrated Control Technology (BADCT),* which is an improvement over BPCTCA that is required for all new industrial plants generating an effluent for the first time.

Effluent limitations for 1977 and new source performance standards (BPCTCA and BADCT, respectively) were based upon three significant pollutant indicators: BOD, TSS, and phenols. The effluent limitations for phenolic compounds were applicable only to the cumene process (bis-phenol A and p-cresol manufacturing). In addition, the 1983 performance standard (BATEA) specified COD as well.

The 1977 standard (BPCTCA) specifies that a biological process (activated sludge, trickling filter, aerated lagoon, or anaerobic lagoon) be used to provide end-of-pipe treatment. With any of these processes, there must be appropriate pretreatment for pH control, equalization, oil and grease removal, etc., in order to limit various waste loads and remove materials that might interfere with the performance of the biological system. In some instances, however, a combination of physical and chemical processes, (for example, activated carbon, ammonia stripping, chemical oxidation, ion exchange, and reverse osmosis) is allowed; or, if waste loads are adequately reduced as part of the industrial process, then biological treatment is not required.

The 1983 standard (BATEA) requires the addition of an activated carbon process following the biological system in order to remove those refractory dissolved organics that have passed through the biological system as well as to remove some biodegradable pollutants that have not been adequately removed in the biological system. Effluent suspended-solids reduction utilizing filtration or coagulation may be required between the biological and carbon systems. Even though the activated carbon process is utilized, it may also be necessary to have the industrial process include certain controls to reduce pollutants: for example,

1. Substitution of noncontact heat exchangers or direct contact water cooling;
2. Use of nonaqueous quench media as a substitute for water where direct contact quench is required;
3. Recycling of process water;
4. Reuse of process water (after appropriate treatment) as makeup to evaporative cooling towers where noncontact cooling water is circulated;
5. Use of process water to generate low-pressure steam by noncontact heat exchangers in reflux condensers of distillation columns;
6. Recovery of spent acids or caustic solutions for reuse;
7. Recovery and reuse of spent catalyst solutions; and
8. The use of nonaqueous solvents for extraction of products.

The end-of-pipe technology for new source standards (BADCT) has been defined as the use of biological treatment followed by suspended-solids removal by clarification sedimentation or by granular media filtration. Exemplary in-plant controls such as the above are assumed to be applicable as well. This is particularly important if constituents are present that might be toxic to the biological system.

V. General Considerations for End-of-pipe Treatment Technology .

The technologies which are now utilized in the organic chemicals industry in the United States and the achievable treatment level which have been proposed by the federal government are as follows:

Biological Treatment Performance

The biological treatment techniques most commonly used by the organic chemicals industry are activated sludge and aerated lagoons. In developing its guidelines for the organic chemicals industry, the federal government relied on the performance records of a number of treatment plants (see Table 6). Data from those judged to be exemplary are summarized below:

	COD Removal *percent*	**BOD Removal** *percent*	**TOC Removal** *percent*	**Effluent TSS** *mg/liter*
Exemplary Single-Stage and Multiple-Stage Treatment Plants	74	93	79	134
Exemplary Single-Stage Treatment Plants	69	92	60	65

Some additional sampling was performed at these plants; the results, which are summarized in Table 7, agree very well with the long-term historical data shown in Table 6. Table 7 also indicates the impact of total dissolved solids and oil on the level of suspended solids. Data from exemplary plants are summarized below:

	COD Removal *percent*	**BOD Removal** *percent*	**TOC Removal** *percent*
Exemplary Treatment Plants	72	87	58

There is growing evidence that high concentrations of total dissolved salts or high levels of oils and greases entering a biological plant contribute to high TSS levels. The effect of salts on a biological treatment system, especially on an activated sludge process, are summarized in Table 8.

Table 6
Historic treatment plant performance 50% probability of occurrence

Plant No.	Treatment System[4]	Category	COD		BOD		TOC		SS		Data Base	
			% Removal	Effluent Mg/liter	% Removal	Effluent Mg/liter	% Removal	Effluent Mg/liter	% Removal	Effluent Mg/liter	Duration (months)	Performance Period
1[4]	AL	D	75	320	97	10	-	-	-	-	6(Sept-Feb)	daily average
2[1 2]	AS-AL	C	96.4	470	-	-	-	-	-	163	12	daily average
3[1]	AS	D	63	200	93.5	16	-	-	-	55	12	monthly average
4[1]	AS	B	64.2	120	-	15	-	-	-	-	14	monthly average
5[1 2]	TF-AS	B	73.5	83	-	-	-	-	-	-	14	monthly average
6	AL	B-C	-	-	-	291	-	-	-	665	12	weekly average
7	AL	C	-	165	-	9.9	-	-	-	81	12	monthly average
8[1]	AL	B	-	75	-	23.5	-	-	-	24.3	12	monthly average
9[1]	AS	C	-	-	83	152	60	170	-	130	7(Aug-Feb)	daily average
10[1]	AS	B	74.5	80	90.1	20	-	-	-	-	12	weekly average
11[1 2]	AS-AL	C	-	-	99.7	20	97	100	-370	145	12	daily average
12	AS	A-B	85	97	-	59	-	-	-	-	12	monthly average
13	AS	B	-	610	-	294	-	295	-	189	14	monthly average
14	AS	B	-	-	73	410	42	780	-	280	14	monthly average
15	AL		-	226	-	63	-	-	-	-	6(July-Dec)	weekly average
16[1]	AS	D	-	-	82.5	362	-	-	-	289	8(Aug-Mar)	monthly average
17[1]	AS	D	67	1,760	-	-	-	-	-	-	6(June-Oct)	daily average
18	AS	D	25.4	1,520	63.6	303	-	-	-	480	12	weekly average
19[1]	AS	D	-	-	97.6	157	-	-	-	-	5(June-Sept)	montly average
20[1]	AS	C	-	296	98.8	46.9	-	-	-	-	5(June-Sept)	weekly average
Exemplary Plant Average			74	378	93	82.2	79	135	-	134		
Exemplary Single Stage Plants - Average			69		92		60		-	65[3]		

---

[1] *Plants considered to be exemplory in performance.*
[2] *Multiple-stage biological treatment*
[3] *Plant 16 is not included in average*

Table 7
Treatment plant survey data[1]

Plant No.	Treatment System[6]	Category	COD		Total BOD		TOC		TSS		TDS	Oil & Grease
			% Removal	Effluent Mg/liter	% Removal	Effluent Mg/liter	% Removal	Effluent Mg/liter	% Removal	Effluent Mg/liter	Effluent Mg/liter	Effluent Mg/liter
2[2]	AS-AL	C	64	2,300	90	427	32	2,710	Negative	4,700	2,300	-
3[2]	AS	D	71	284	73	74	71	132	Negative	62	3,100	1[3]
4[2]	AS	B	57	214	82	13	35	80	40	14	2,900	4[3]
5[2]	TF-AS	B	59	133	92	12	43	61	97	44	1,430	2[3]
6	AL	B-C	66	980	73	235	11	573	Negative	362	3,000	11[3]
8[2]	AL	B	69	92	84	6	26	52	99	3	690	-
9	AS	C	75	595	92	75	69	242	Negative	50	3,810	12[3]
11[2]	AS-AL	C	94	337	99	16	27	343	Negative	145	2,690	1[3]
13	AS	B-C	65	940	90	177	64	470	120	338	1,520	6[3]
16[2]	AS	D	54.8	1,650	82.1	300	80.8	280	43.6	552	10,990	226[4]
17[2]	AS	D	60	1,400	81.4	240	63.4	410	Negative	1,300	3,750	24[4]
			77.3	1,000	90	310	76.8	360		732	4,060	22[4]
18	AS	D	22.1	2,680	16.7	650	-	1,025	42.9	1,170	2,050	106[4]
19[2]	AS	D	59.5	5,100	69.8	1,800	55.8	1,700	Negative	2,500	8,360	-
20[2]	AS	C	96.2	317	99.5	19	96.6	114	Negative	100	1,950	19[4]
21	AL	C	62	600	78	27	66	47	89	30	9,800	-
22	AS	B	16.1	1,370	47.5	210	8.3	550	53.4	82	15,400	<.03[4]
23	AS	B	95.4	147	92.6	41	95.4	35	Negative	37	580	21[4]
Average[5]			72		87		58					

---

[1] *Based on 24 hours composit samples.*
[2] *Plants considered to be exemplary in performance based on historical data.*
[3] *Oil and grease are reported as carbon tetrochloride extractables.*
[4] *Oil and grease and reported as Freon extractables.*
[5] *Includes exemplary plants as well as Plant 23.*
[6] *AL - aerated lagoon*
AS - activated sludge
TF - trickling filter

Granular Media Filtration

The present use of granular media filters is very limited in the organic chemicals industry. However, many industries are in the process of installing these filters in order to meet effluent limits for TSS. The selection of media types and the addition of chemicals can substantially influence the quality of the final effluent, and it is generally assumed that effluent suspended solids can be reduced to a range of 5 to 30 mg/liter (50 to 90 percent removal) through the use of these filters. Some samples collected from organic chemical plants were tested for suspended solids removal. The results, shown in Table 9, indicate that filtration removed an average of 20% COD, 17% BOD, and 20% TOC.

Activated Carbon Adsorption

Granular activated carbon technology has been extensively studied in the United States for several years. Although it seems feasible on a small scale, many problems develop in full-scale situations. For example, there are high attrition losses of carbon due to mechanical grinding and other materials handling problems. Moreover, precise and dependable methods of operating the regeneration furnace have yet to be developed. Another problem is that many low molecular weight compounds are not amenable to adsorption on activated carbon. The clogging and substantial increases in head loss across the carbon column, which are caused by TSS of more than 50 mg/liter and by more than 10 mg/liter of oils and greases applied directly to carbon beds, are also matters of concern.

Table 8
Effects of total dissolved inorganic solids on biological system performance

Salt Concentration	Effects on Biological System
500 - 2,500	Optimum Activity
2,500 - 5,000	Slight Increase in Effluent Suspended Solids
5,000 - 8,000	Suspended Solids in Effluent Settleability Decreases Slightly
8,000 - 12,000	Significant Effluent Suspended Solids Settleability Poor
12,000 - 15,000	High Concentrations of Effluent Suspended Solids. Difficult to Operate Activated Sludge. Effluent Soluble BOD Increases Settleability Very Poor
15,000	Severely Toxic

Table 9
Removal by Filtration
(Performed on Biological Treatment Plant Effluent)

Plant	% COD	% BOD	% TOC
3	9	4	3
15	87	56	78
15	85	—	82
14	24	28	14
9	11	—	5
9	10	—	17
13	32	36	8
4	—	—	—
24	8	2	20
12	21	—	7
21	3	—	8
16	84.3	57.8	75.9
25	39.3	—	39.4
20	8.5	17.2	33.0
35	51.4	—	27.7
26	26.2	71.4	41.2
27	—	12.5	25.0
18	86.8	72.1	90.6
17	88.4	55.6	91.6
19	33.3	—	66.0
Average[1]	20	17	20

---

[1] *Average does not include plants 15, 16, 17, 18, and 26, since these plants have excessively high effluent TSS and would bias the results*

The results of a survey at six activated carbon plants treating raw organic chemical wastewaters are shown in Table 10. Based on these data and on small-scale laboratory studies, the average performance for activated carbon systems was determined to be as follows:

Parameter	Carbon Exhaustion Rate lb. Removed/lb. Carbon	Soluble Removal %
COD	0.41	69
BOD	0.03	20
TOC	0.06	87

VI. Effluent Limitations From the Various Technologies

In reviewing the above data, the federal government arrived at percentage removal factors and minimum concentrations that could be achieved through the application of the technologies discussed above. These levels are summarized below.

BPCTCA Treatment Systems - 1977 Standard

The following pollutant reduction factors are considered achievable with BPCTCA treatment technology:

	Reduction Factors		Best Achievable Under Worst Conditions mg/liter[3]
	Range	Average	
BOD[1]	83-99%	93%[2]	20
COD	63-96%	74%[2]	—
TSS	reduced to 65 mg/liter[3]		30

[1]Controlling Parameter
[2]Annual Average
[3]Monthly Average

Table 10
Activated carbon plants treating raw wastewaters

Plant	Pretreatment	Removal Efficiencies %		Flows-gpd		Hydraulic Loading gpm/sq. ft.		Contact Time-minutes		Carbon Exhaustion Rate	
		Design	Present	Design	Present	Design	Present	Design	Present	Design	Isotherm
28	Solids Removal and Equalization 9-hr. detention time	—	Polyol-11	100,000	55,000	5.6	3.0	22	40	$\frac{\text{0.4 lb. polyol}}{\text{lb. carbon}}$	—
29	Equalization 150-day detention time	TOC-94	TOC-89	20,000	7,000	0.49	0.17	540	1,550	$\frac{\text{0.07 lb. TOC}}{\text{lb. carbon}}$	$\frac{\text{0.19 lb. TOC}}{\text{lb. carbon}}$
30	Equalization, Neutralization and solids removal	Phenol-89	Phenol-94	750,000	500,000	4.6	3.1	60	104	$\frac{\text{.028 lb. phenol}}{\text{lb. carbon}}$	—
31	Equalization and Neutralization	—	TOC-91	30,000	20,000	—	—	660	912	—	—
32	Equalization and Neutralization	Phenol-99.9	Phenol-95	72,000	22,000	2.0	0.6	215	75	—	—
33	Equalization, Neutralization and solids removal	Color-90	—	800,000	—	7.7	—	27	—	$\frac{\text{5.4 lbs. color}}{\text{lb. carbon}}$	—

Federal permits for BPCTCA have generally been granted on the basis of a plant's achieving 93 percent removal of BOD on an annual basis. This allows, under worst winter conditions, a monthly average of 2.1 times the annual average and a maximum daily discharge of 3.9 times the annual average. Although this approach works well in many cases, in others—for example, multi-product, batch-operated, and campaign-scheduling industries—it is not satisfactory, and generalized approaches have not proven to be successful.

BATEA Treatment Systems - 1983 Standard

Based on previous performance data for multiple-stage biological treatment plants, existing carbon treatment plants, and laboratory carbon data, waste reduction factors were formulated by the federal government for BATEA as follows:

Parameter	Reduction Applied to BPCTCA Effluent Limitations	Best Achievable Under Worst Conditions mg/liter[2]
BOD	90%[1]	10
COD	60%[1]	50
TSS	reduced to 15 mg/liter[2]	10

[1] *Annual Average*
[2] *Monthly Average*

The affected industries do not agree with the limitations, claiming that there is not yet enough known about carbon technology.

BADTC Treatment Systems - New Sources

Based merely on filtration test data, the federal government proposed the following reductions for BADTC technology:

Parameter	Reduction Factors Applied to BPCTCA Effluent Limitations	Best Achievable Under Worst Conditions mg/liter[2]
BOD	17%[1]	10
COD	20%[1]	—
TSS	reduced to 10 mg/liter[2]	10

[1] *Annual Average*
[2] *Monthly Average*

VII. Summary

Since all of the above recommendations were made by the federal government primarily on the basis of its own studies, many questions still remain within the organic chemicals industry regarding final effluent limitations. Since the industry cannot be standardized, it is unrealistic to attempt to establish guideline limitations that are applicable to every industrial plant within each subcategory. Because of this complexity, each permit is generally evaluated on a case-by-case basis using the guidelines as a starting point. One key factor not considered by any of the guideline studies is the incorporation of effluent variability into the permits. For the organic chemicals industry, in which most of the biodegradable materials are soluble, many operational constraints and environmental conditions influence the variability of the final effluent. For example, during cold weather, the effluent will deteriorate because the biological organisms cannot perform as they do in warm weather. Therefore, the permits must be based on worst conditions, i.e., worst winter situations anticipated during the life of the permit. This is a subject currently under discussion between industry and the government. In addition, because small industrial plants do not have the capability to reduce wastewater flows on the same level as the larger plants, they have been penalized more severely. Industrial plants that are multi-product in nature and employ batch processes have much higher variability in raw waste characteristics; consequently, their treatment facilities are subject to varying wastestreams, which results in much more variable effluents than those of continuously operated industries. Finally, those industries that manufacture products as orders come in are subject to campaign scheduling in order to meet requests from their customers; such campaign scheduling can cause significant variability in the quality of the raw waste and therefore of the treated effluent.

Because of the above considerations and the difficulties encountered in attempting to secure workable yet controllable permits, many problems have arisen with respect to the organic chemicals industry's efforts to comply with pollution abatement goals. There is no doubt that the technology will eventually develop to allow industry to construct economically feasible treatment systems that are capable of upgrading the water quality in the United States and of being monitored satisfactorily by the government.

Acknowledgements

The majority of the information contained in this paper was taken from the April, 1974, publication, "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the MAJOR ORGANIC PRODUCTS Segment of the Organic Chemicals Manufacturing, Point Source Category," based on a study conducted by Roy F. Weston Company for the U.S. Environmental Protection Agency. The purpose of the study was "to establish effluent limitations guidelines for existing point source discharges and standards of performance and pretreatment standards for new sources."

All of the tables except Table 8 were taken from the above referenced publication.

Biochemical Treatment of Highly Concentrated Wastewaters from Wool-Scouring Operations

**Skirdov I.V., Shvetzov V.N.,
Morosova K.M., Gubina L.A.**

The problems associated with highly concentrated wastewater treatment are becoming more noticeable today. A typical example of a given type of wastewaters is a highly concentrated wastewater generated from wool scouring plants. The wastewaters contain substantial amounts of wool grease, wool, various impurities, dissolved organic and inorganic matter. The concentration of suspended solids is up to 20 g/l, organic concentration varies ranging from 10 to 35 g/l. COD and from 5,0 to 20 g/l total BOD. At present mechanical, chemical, physical-chemical and biological treatment processes are being used to treat wool scouring operation wastewaters. In spite of a variety of treatment methods, these wastewaters present certain treatment problems. Chemical treatment process requires the use of expensive chemicals, careful control of the process and accurate dosing of reagents, resulting in large production of waste sludge. At the same time the area for application of anaerobic Biological treatment in digesters is broadening due to ease of operation, reduced production of sludge and efficiency. The BOD limit in treated effluent from digesters varies ranging from 800 to 1000 mg/l, therefore effluent requires final treatment. It should be noted that digestion detention period of 20 days is needed to produce an effluent with a total BOD of 8000 to 1000 mg/l. In practice, existing digesters are designed with detention period of 8-10 days, resulting in effluent with a total BOD of 1500 to 2000 mg/l, then effluent should be treated in municipal biological treatment plants (Fig 1, Scheme 1).

However in most cases the treatment capacity of municipal treatment plants doesn't meet existing standards and isn't sufficient to handle wool-scouring wastewaters without additional dilution after pretreatment in digesters. It makes us seek ways of final wastewater treatment prior to their discharge into municipal sewerage system or to receiving waters.

The institute VODGEO has carried out studies on the feasibility of wool-scouring wastewaters treatment in digesters followed by final treatment in aeration tanks without dilution as well as complete biological treatment under aerobic conditions. Studies were conducted on natural wastewaters generated from worsted factory where they are treated by using soap and soda.

Experiments were carried out on laboratory scale continuous flow models of digesters and complete mixing aeration tanks. The facilities performance was monitored by analyses of COD and total BOD, pH, volatile fat acids concentrations, the N and P content, concentration of ether-soluble material, anaerobic and aerobic activated sludge concentrations, quantity and composition of gas produced from digesters. In order to obtain the criterion for adequate evaluation of digesters performance as well as for quantitative evaluation of biodegradable substrate in digesters determinations of influent and effluent BOD from digesters have been conducted according to special procedure.

As digesters are completely mixed biological reactors, oxidation rate is determined on the basis of effluent substrate concentration. The relationships between oxidation capacity of digester and specific oxidation rate and effluent organic concentration were found experimentally; oxidation capacity and specific oxidation rate increase with decreasing the degree of treatment. It has been found that the effect of effluent organic concentration and volatile fat acid concentration on specific oxidation rate is expressed by hyperbolic function (Fig. 2) and may be described by Michaelis-Menten expression for fermentation reactions.

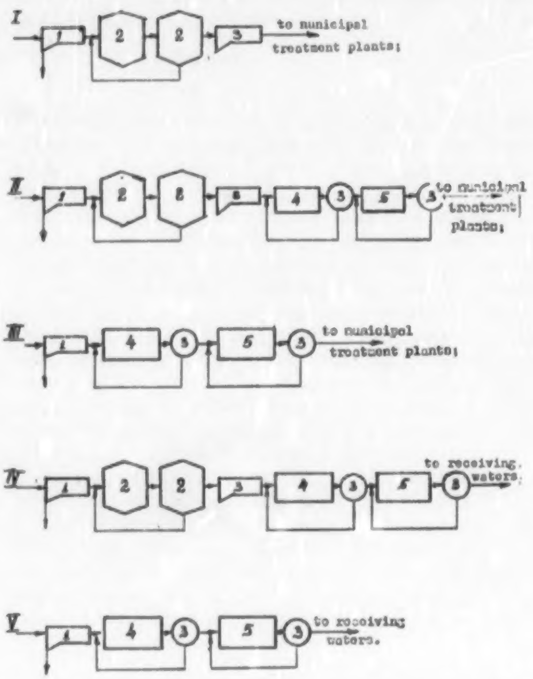

I
1
2
2
3
to municipal treatment plants;
II
1
2
2
3
4
5
5
5
to municipal treatment plants;
III
1
4
5
5
5
to municipal treatment plants;
IV
1
2
2
3
4
5
5
5
to receiving waters.
V
1
4
5
5
5
to receiving waters.

Figure 1. Biological treatment schemes for wool-scouring operation wastewaters
1. **Primary settling tanks;**
2. **Digestion tanks;**
3. **Final setting tanks;**
4. **- first-stage aeration tank;**
5. **- second-stage aeration tank;**

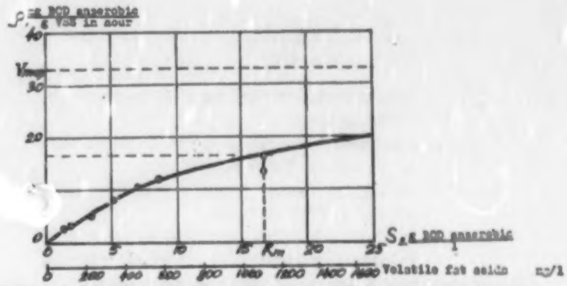


Figure 2. Specific oxidation rate versus organic concentration (on BOD basis) and volatile fat acids concentration in effluent

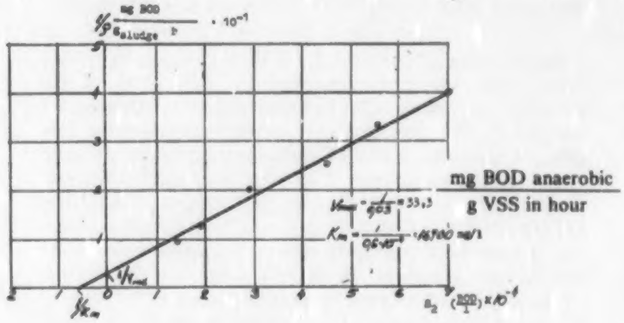


Figure 3. Binary reciprocal values graph of relationship between specific oxidation rate and organic concentration in effluent from digesters.

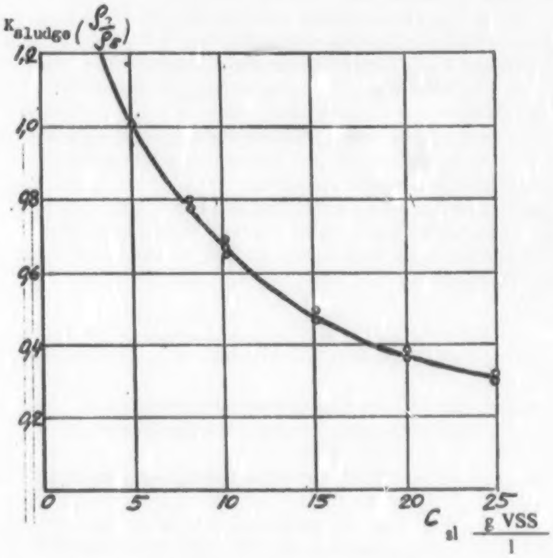


Figure 4. Relationship between coefficient K_{sludge} and anaerobic activated sludge concentration

$$\mathcal{S} = \frac{V_{max}[S_2]}{K_m + [S_2]}$$

where: $\mathcal{S}$ — specific oxidation rate; mg BOD anaerobic per g VSS in hour

S_2 — substrate concentration, mg BOD anaerobic/ l or mg volatile fat acids 1/l.

V_{max} — maximum reaction rate, mg BOD anaerob per g VSS in hour.

K_m — Michaelis-Menten constant expressed as substrate concentration at which reaction rate is equal to half the maximum rate.

Method of binary reciprocal values was used to define V_{max} and K_m. It can be seen from Fig. 3, that maximum specific oxidation rate of wool scouring wastewaters in digesters is 33.3 $\frac{\text{Mg BOD}}{\text{g VSS}}$ • h, k_m is 16700 mg/l.

As the value of constant K_m is dependent on its nature rather than substrate concentration, high value of K_m obtained for treated effluent from digesters indicates the complexity of wool-scouring wastewater composition. The effect of anaerobic activated sludge concentration on basic technological parameters has been investigated for the purpose of improving digester performance. Oxidation capacity of digesters and the degree of treatment considerably increase with increasing activated sludge dosage while specific rate decreases. However it decreases slower than increases activated sludge concentration due to overall oxidation rate increases. The decrease in specific oxidation rate with increasing sludge dosage appears to be accounted for changes in prebacterial film under hydrodynamic conditions that in turn prevents feeding of substrate to microorganisms and inhibits metabolism.

In order to define the relationship between anaerobic activated sludge concentration and specific oxidation rate coefficient K_{sludge} have been suggested.

Coefficient K_{sludge} is equal to the ratio of specific rate at a given sludge concentration to rate at sludge concentration of 5 g VSS/l.

It has been proven that coefficient K_{sludge} doesn't depend on substrate concentration, but depends only on anaerobic activated sludge concentration (Fig. 4).

Taking into account specific oxidation rate and coefficient K_{sludge} technological parameters of digesters treating highly concentrated wastewaters should be calculated by using the equation:

$$T = \frac{S_o - S_t}{\mathcal{S} \cdot C_{sludge}(1 - \quad) \cdot K_{sludge}}$$

where: T = detention period in digesters, days.

S_o = organic concentration in influent, mg/l total BOD.

S_t = effluent organic concentration mg/l total BOD.

$\mathcal{S}$ = specific oxidation rate at sludge concentration on VSS 5 g/l, mg total BOD per g VSS.

= ash content in sludge, parts/unity.

K_{sludge} = coefficient considering effect of sludge concentration on its activity, determined experimentally.

The studies on the final treatment of wool scouring wastewaters have shown that treated effluent from digesters with unoxidized organic material content of 3000 mg/l on a total BOD basis, can be treated successfully without dilution in complete mixing aeration tanks, operating according to a two-stage scheme.

It is evident from Fig. 5 that oxidation kinetics of wool-scouring wastewaters in complete mixing aeration tanks can be described by Michaelis-Menten expressions for fermentation kinetics.

The values of kinetic constants (Fig. 6,7) have been found experimentally and may be used to calculate basic technological parameters of aeration tank performance.

With reference to Fig. 6, 7, it can be seen that maximum specific oxidation rate in a first-stage aeration tank is 55.5 $\frac{\text{mg BOD}}{\text{g VSS hour}}$ hour and in a second-stage aeration tank is $\frac{\text{mg BOD}}{\text{g VSS h}}$

The value of constant K_m for the first-stage aeration tank is higher than that for the second-stage aeration tank and is equal to 83.5 mg/l and 13.8 mg/l, respectively. From data obtained, it can be concluded that high oxidation rate occurs in the first stage aeration tank because activated sludge is under conditions of excess substrate. At the second stage the required degree of treatment is achieved at lower oxidation rate due to lack of sufficient amount of substrate. At each stage in aeration tank the development of specific microorganisms takes place due to autoselection of microorganisms acclimitized to given conditions and mutant changes in the culture. In its turn it affects both physical properties of activated sludge (in particular, its settling properties) and kinetics of biochemical treatment process. In the first stage if amount of substrate isn't limited, autoselection of microorganisms takes place promoting increase in maximum oxidation rate, and at the second stage if amount of substrate is limited the development of the culture encourages reduction in K_m value and more full substrate utilization. So the division of the process into two stages improves process efficiency at the first stage and provides more full oxidation of organic matter at the second stage.

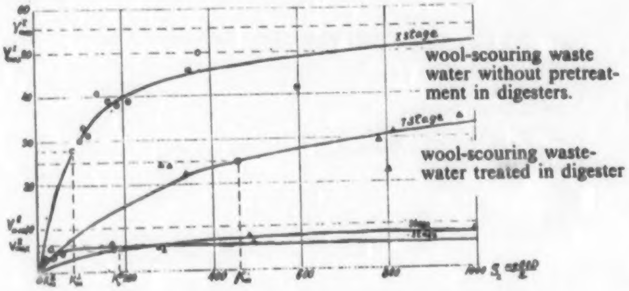


Figure 5. Relationship between specific oxidation rate in first-stage and second-stage aeration tanks and effluent organic concentration.

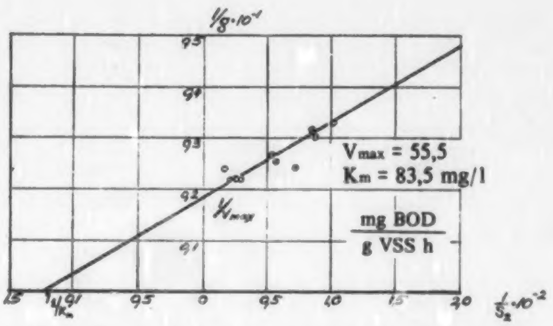


Figure 6. Binary reciprocal values graph of relationship between specific oxidation rate and effluent organic concentration from first-stage aeration tank.

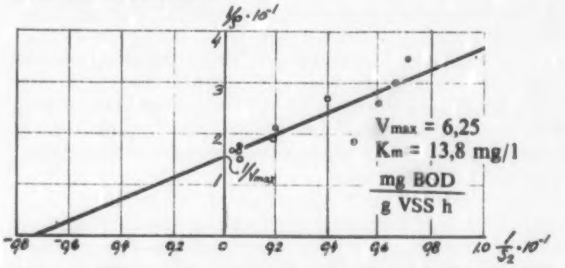


Figure 7. Binary reciprocal values graph of relationship between specific oxidation rate and effluent organic concentration from second-stage aeration from second-stage aeration tank.

Laboratory studies of aerobic treatment of wool scouring wastewaters demonstrated the feasibility of their treatment in two-stage completely mixed aeration tanks without preliminary anaerobic digestion and dilution.

The results of kinetic studies on oxidation of wool-scouring waste waters with a total BOD of 8000 to 9000 mg/l in completely mixed aeration tanks are presented in Fig. 5. From data obtained it is evident that oxidation kinetics of these wastewaters also depends on laws of fermentation kinetics and may be described by Michaelis-Menten expressions. Kinetic constants V_{max} and K_m are $\frac{\text{50 mg BOD}}{\text{gVSS in hour}}$ and 460 mg/l for the first stage aeration-tank, $\frac{\text{10 mg BOD}}{\text{gVSS in hour}}$ and 185 mg/l, for the second stage aeration tank, respectively. From Fig. 5, it is seen that pretreatment of wastewaters has a marked effect on oxidation kinetics in aeration tanks. There is a significant difference between values for constant K_m(83,5 mg/l instead of 460 mg/l for the first-stage aeration tank and 13,5 mg/l instead of 185 mg/l for the second-stage aeration tank). In its turn, it affects specific oxidation rate, for instance, wastewater treated in anaerobic digester to a total BOD of 200 mg/l will be oxidized at the rate of $\frac{\text{39,2 mg BOD total}}{\text{g VSS hour}}$ in the first aeration tank, while without pretreatment they will be oxidized at the rate of $\frac{\text{15.2 mg total BOD}}{\text{g VSS h}}$

It might be explained by the fact that during the destruction organic pollutants are broken down to simpler organic structures thus providing more fast aerobic oxidation.

The studies conducted have made it possible to carry out the comparative analysis of various treatment schemes for wool-scouring operations wastewaters.

For technical-economic comparison the following treatment schemes have been chosen (Fig. 1):

I - Preliminary anaerobic treatment in digesters followed by final treatment in municipal biological treatment plants.

II - Preliminary two-stage anaerobic- aerobic treatment producing effluent with a total BOD of 200 mg/l followed by final treatment in municipal biological treatment plants.

III - Preliminary two-stage aerobic treatment producing effluent with a total BOD of 200 mg/l followed by final treatment in municipal treatment plants.

IV - Complete two-stage anaerobic-aerobic treatment reducing a total BOD to 15 mg/l.

V - Complete two-stage aerobic treatment producing effluent with a total BOD of 15 mg/l.

For a comparison wool-scouring wastewater flow is taken as 2000 m/days, municipal wastewater flow as 5000 mg/days, pollutant concentration in incoming wool-scouring wastewaters is in the range from 8000 to 9000 mg/l on the total BOD basis, the total BOD of untreated municipal wastewaters is 200 mg/l.

Preliminary evaluation of technical and economic feasibility of anaerobic-aerobic and two-stage aerobic treatment processes allowed to define optimum relationship between stages of both schemes and appropriate optimum technological parameters of facility performance.

The organic concentration in treated effluent from digesters is taken as 3000 $\frac{\text{mg BOD total}}{\text{l}}$, from the first-stage aeration tank in the II scheme is 400 $\frac{\text{mg BOD total;}}{\text{l}}$ in the III scheme 1000 $\frac{\text{mg BOD total;}}{\text{l}}$ in IV and V schemes $\frac{\text{200 mg BOD total,}}{\text{l}}$ anaerobic activated sludge concentration is 20 g/l, aerobic activated sludge concentration in the first-stage aeration tank in II and IV schemes is 4,5 g/l, in III and IV schemes is 10 g/l, in the second-stage aeration tank in all schemes is 4,0 g/l.

For approximate economic comparison minimum total volume of facility was assumed to be a criterion of economic effectiveness of treatment schemes because on the basis of preliminary evaluation, comparative costs of digesters and aeration tanks are almost equal. From Table 1, where facility volumes are given for each scheme, it may be concluded that II, III and IV schemes are most advantageous.

However it should be noted that the treatment process of wastewaters has been evaluated without consideration of sludge treatment.

It also should be noted that activated sludge production is lower in an anaerobic digester than that in an aeration tank, therefore II and IV schemes with digesters may be expected to be the most advantageous so the combination of anaerobic and aerobic process used for treatment of highly concentrated wastewaters allows advantages of each method to be used more fully and shortcomings to be eliminated, thus enhancing effectiveness and efficiency of the treatment process as a whole

Table I. Technical-economic comparison of biological treatment schemes for wool-scouring operation wastewaters

Treatment unit	Digestion tank	First-stage aeration tank	Second-stage aeration tank	Municipal treatment plants	volume (cu m)
Scheme	Volume (cu m)				
I	15000	-	-	3800	18800
II	4000	1230	900	630	6760
III	-	2700	3560	630	6900
IV	4000	1560	1200	-	6760
V	-	7700	1200	-	8900

Analytical and Process Improvements in Biological Treatment of Municipal Waste Waters

William J. Love

The operation of biological wastewater treatment plants is a complicated process requiring the blending of interdisciplinary professions, skills and experience. To managers responsible for the operation of wastewater treatment programs, the biological treatment process appears to be an all too delicate, sensitive and often elusive process. Yet, the biological treatment process still remains today, sixty years after its innovation, as the most economical and widely used type of secondary treatment for large municipalities. This continued popularity has resulted from the biological process' ability to consistently produce good quality effluents when properly operated and controlled. The emphasis here is on operation and control; the key to successful operation of a biological treatment plant is extensive analytical and process control. The analytical investigations must completely characterize all wastewater parameters and also each step of the biological treatment process. The process control must incorporate the analytical results into an operational program based on the biological-chemical-physical principles of microorganisms metabolism and liquid-solids separation. The analytical and process control programs must be flexible to meet the ever changing conditions within a plant, and must be continually reevaluated and revised to meet the increasing growth of wastewater flows.

The intent of this presentation is to discuss my organization's experience in operating biological treatment plants, to outline our analytical and process control programs, and to discuss the role of analytical and process control in solving some of the peculiar problems which have occurred in our biological treatment plants.

Process Control Program

A process control program in a biological treatment plant involves the collection and analysis of representative samples of waste and process flow throughout the plant; monitoring and controlling critical process functions and variables according to established principles; recording and evaluating historical data for use in predicting trends and process modification requirements; and conducting experimental investigations with process modifications, and even with entirely new processes for solving treatment problems. Our own process control program can best be explained by example using one of our biological plants treating a high strength industrial waste.

This plant is a 10 MGD activated sludge plant which treats a brewery waste having a 1000 mg/l BOD concentration and comprising 75% of the total influent plant loading. The plant has screening, grit removal, primary gravity clarification, large 13 hour detention complete mix aeration tanks, final gravity clarification with low surface loading rates of 360 gpd/square foot, and chlorine disinfection. Sludge handling is by gravity thickening, centrifugal dewatering and multiple hearth incineration. Although the plant's BOD removals have been excellent, the activated sludge process produces a very light sludge floc which is difficult to separate in the final clarifiers and which results in the plant's not meeting expectations. A tremendous amount of analytical, process control and experimental work has been performed attempting to improve the settling characteristics of this activated sludge system.

Daily samples of the individual brewery, domestic and combined plant influent wastes are composited proportional to flow and analyzed for such parameters as TSS, SS, VSS, BOD, COD, TOC, TKN, NH^{3}-N, ortho PO^{4}, D.O., pH, temperature and turbidity. Daily samples are also composited from each major step in the treatment process so as to completely depict all waste and process parameter changes occurring throughout the treatment process. These inter-process samples are taken at points including the primary clarifier effluent, aeration tank influent and effluent, final clarifier effluent, chlorine disinfection effluent, primary sludge, return and waste activated sludge, thickened sludge, gravity thickener supernatant, and centrifuge centrate; and are analyzed for parameters similar to those already mentioned. In addition, a daily microscopic examination of the biomass is made and the predominant microorganisms present are identified and observed for change. All effluent and process flows are metered and recorded. The above information is used to provide a detailed description of the process loadings throughout the plant so that the biological process can be adjusted to remain within established limits for effective treatment control. This data is also used to routinely prepare solids balances around the activated sludge system for controlling the return and waste activated sludge flow rates from the final clarifier and the overall sludge handling requirements of the plant.

In addition to the complex analytical work performed in the laboratory, the plant operators periodically perform simpler tests to closely monitor several critical functions in the plant. These tests include conducting dissolved oxygen profiles of the aeration tanks to insure that there is sufficient oxygen present; measuring oxygen uptake rates of the activated sludge biomass as an indicator of changing conditions such as influent shock loading or toxic wastes, monitoring aeration tank and return sludge concentrations using laboratory centrifuges; performing settleometer tests of the aeration tank effluent to measure the activated sludge's settling characteristics; and measuring the depth of clear water in the final clarifiers to the sludge blanket to indicate the overall settleability and solids balance in the system. All of the above tests are performed every two hours to four hours and provide an accurate picture of existing plant conditions. These simple tests often serve as early warning indicators of impending process upsets and allow the plant personnel to take corrective actions before the final effluent deteriorates.

This plant has had continued difficulty in producing a satisfactoy settling activated sludge floc in spite of all the close attention to monitoring and controlling the biological process. Therefore, the plant's process control program was expanded to try several process modifications. One of the first was the addition of inorganic salts and organic polyelectrolyites to the aeration tank effluent in an attempt to weight down the sludge floc in the final clarifiers. This proved to be not only far too expensive, but also not too effective for this industrial waste. Alum addition to the primary clarifiers at a feed dosage of 100 mg/l produced an extremely clear primary effluent and resulted in overall primary removals of 80% SS and 40% BOD, but there were no benefits observed in the activated sludge system. Chlorine and hydrogen peroxide addition to the return activated sludge were tested for controlling filamentous microorganisms, but this proved to have no beneficial effect. The final clarifiers were modified with the addition of mechanical mixers and picketts to promote better flocculation of the activated sludge floc, but this did not produce better settling. One of the more recent process control modifications has been the conversion of the complete mix aeration system to a plug flow aeration system in an attempt to influence the biological metabolism rate and shift the microorganism predominance away from the filamentous and lower microorganisms. Consideration is now being given to a further conversion of the aeration tanks so that a sludge reaeration system can be evaluated. Nutrient addition in the form of nitrogen, phosphorous, and trace metal supplements have been evaluated due to the industrial waste's natural deficiency in these substances, and this investigation is continuing. Each of the above process modifications requires months for conducting a complete research investigation and full scale plant trial. This work requires considerable additional laboratory analytical work and operational monitoring for a thorough evaluation of the testing program.

In addition to the full scale plant process modifications discussed above, our process control program has also included a considerable amount of pilot scale testing and bench scale experimental work. Several long term scale model pilot reactors have been operated to investigate all aspects of aerobic biological treatment of this brewery-domestic waste. This pilot work has investigated the effects of aeration detention time, biomass concentration, sludge age, chemical and nutrient additions, oxygen and mixing intensities, pH adjustment and shock loading susceptibility. Pilot work was also performed using ultra sonic sound generation in an attempt to alter the activated sludge floc structure, causing it to degasify and thereby improving its settleability. In this work, which showed no overall benefit, lower frequencies tended to improve the initial settling rates while higher frequencies tended to mix the sludge and completely prevent settling. Several solids separation processes have been piloted to be used either as an alternative or in conjunction with gravity clarification of the activated sludge. One of the processes piloted, floatation separation, proved to be a fairly successful method of activated sludge solids separation but proved to be unfeasible due to the large area requirements needed. Also, this method would have required an additional solids removal step such as microscreening to meet the effluent requirements. Another piloted process, mixed media filtration, was rejected because it required more backwash water than the total plant influent. Still another piloted process, dilution of the final clarifier influent mixed liquor suspended solids by an intermediary Sweco centrifugal solids separator, has proven to be both feasible and to improve the settling characteristics of the diluted sludge in the final clarifiers. The centrifugal solids separator appears to selectively classify the biological solids so that the filamentous microorganism count in the final clarifiers is reduced. Our process control investigations at this plant are continuing with both full scale and pilot testing.

Another problem caused by septic sewage is that it does not respond to treatment by the activated sludge process as rapidly as fresh sewage. This condition required a major deviation at our 24 MGD contact stabilization activated sludge plant from conventionally established process control for contact stabilization plants. The septic sewage at this plant receives no primary clarification and would turn the influent ends of the contact aeration tanks black. We were unsuccessful in developing a viable biomass in the aeration system as long as we attempted to operate the plant around conventional parameters of fifteen to forty-five minutes detention time in the contact zone. Laboratory pilot scale and full plant testing indicated that a considerably longer contact time was required to allow the microorganisms to assimilate the septic waste. The treatment process was modified to provide a minimum of two hours detention time in the contact aeration tanks, and immediately a viable biomass developed. This resulted in good treatment performance and a good effluent. Higher air supply rates are required to maintain adequate dissolved oxygen in the contact aeration tanks, and a longer proportion of the aeration system must be devoted to contact aeration rather than stabilization aeration than was originally designed.

The second process control problem caused by our force main system is that the plants experience a severe diurnal flow pattern. In a force main system flow is immediately received at the plant when outlying pump stations are operating. This eliminates any flow lags and dampening such as are experienced in gravity collection systems. We receive very high flows during the daytime and virtually no flow at night, and the switch from high flows to low flows occurs rapidly within an hour as people go to bed and get up. Using our 24 MGD contact stabilization plant as an example, the present average daily flow is 16 MGD, but the daytime flow rate from 6:00 A.M. to midnight is 20 MGD and the nighttime flow rate from midnight to 6:00 A.M. is only 4 MGD. Process control problems arise in trying to maintain a constant solids balance around the aeration system. If the return sludge flow rates are not carefully adjusted to match the widely varying influent flow rates, the solids concentration in the contact aeration tanks will significantly increase during early morning—low flow periods. Later, the high flow surges occurring at 6:00 A.M. wash out the contact aeration tanks and exceed the solids loading capacity of the final clarifiers. More poundage of solids are put into the final clarifiers in a short period of time than can be removed by, the return sludge flow, resulting in the final clarifiers filling up with solids and dumping. Adjustment of the final clarifier return sludge flow rates to compensate for the varying influent flows is difficult due to the wide variation in the liquid hydraulic levels in the siphon suction drawoff type final clarifiers. Process control to prevent solids dumping at this plant requires attention to clarifier sludge blanket depths and influent and return sludge flow rates. In order to expand the usable capacity of the plant and to remedy some of the hydraulic variation effects, we are considering the installation of additional final clarifiers to handle above average daytime flows and also upstream holding tanks to help equalize the flow between daytime and nighttime.

Foaming

A problem which recently developed at one of our activated sludge plants is the production of a heavy, voluminous foam in the aeration tanks. The foam is dark and greasy and cannot be dissipated with the usual spray water. The foam, containing considerable solids, will overflow the aeration tanks and literally spread across the plant site if unchecked, causing nuisance and odor conditions. The foam causes a thick greasy scum to form on the final clarifier surfaces which often spill over into the effluent. The foaming material is incorporated into the mixed liquor and lessens its density, thus decreasing the sludge's normal settleability. The anaerobic digestors have also experienced a severe foaming problem during this time. It was initially believed that the foaming was due to the activated sludge system's sludge age, but exhaustive process control proved this not to be so. Attention was then diverted to the possibility of influent synthetic detergents or other industrial wastes, and an extensive analytical waste monitoring program was initiated to identify the causative agent and locate its source. The analytical tests included oil, grease, ionic, nonionic, and cationic detergent determinations for the plant flows and selected industrial contributors. After considerable research effort, we have concluded that it is not a single factor such as oil or grease causing the foaming problem, but more likely a combination of factors. After several exasperating months of having foam and sludge moving around the plant grounds, we found a fairly economical commercial defoaming agent. This defoamer reduces the foam level in the aeration tanks to an acceptable level and prevents its overflowing. However, we've felt that this is only treating the symptoms and is not a corrective process control measure. Some interesting recent outside research indicates that a particular foam producing bacteria, actinomycetes, may proliferate in activated sludge systems where there is no anaerobic digestor supernatant returned to the activated sludge system. This research indicates that anaerobic digestors produce a toxic agent which prevents actinomycetes growth and foam production in most plants. As a possible coincidence, we had discontinued returning anaerobic digestor supernatant to the activated sludge system at this plant two months before the foaming first occurred. We have now reinstituted a program of limited digestor supernatant return to the aeration system, but since the plant's own anaerobic digestors are themselves foaming, the test supernatant is being trucked in from another plant.

Capacity Upgrading

The need arose at another of our activated sludge plants to double the existing treatment capacity before construction of the expansion facilities could be completed. The original facility treating domestic wastewater had a 5 MGD capacity and utilized a conventional plug flow activated sludge system with both primary and final gravity clarifiers. The plant was required to produce a 20 mg/l SS and BOD effluent. Considerable bench and full scale pilot work was undertaken to investigate alternatives for increasing the plant's capacity. The method selected for increasing the capacity was to institute a process modification and to exert close process control over the entire plant operation. The aeration system was changed from the plug flow mode to a contact-stabilization system. Incidentally, this change resulted with our having an empty aeration tank left over. Alum and polyelectrolyte feed facilities were installed, and alum was added to the contact aeration tank at a point providing fifteen minutes detention in the tank. The mixing in the contact aeration tank provided excellent flocculation with an alum feed dosage of only 25 mg/l., and a small, densely compacted activated sludge-alum floc was produced. An organic polymer at a dosage of 1 mg/l was added to the contact aeration tank effluent at a manhole just prior to its entering the final clarifiers. The flow's gentle roll in the manhole and clarifier influent structures provided adequate flocculation of the activated sludge-alum-polymer floc. The result was a large dense floc which rapidly settled in the overloaded final clarifiers, then being operated at a surface loading rate of 1100 GPD/square foot. The small alum dosage used did not create a measurable increase in sludge production, and the overloaded anaerobic digestors were able to handle the sludge without any adverse effects. Overall, the process was very stable and reliable but required close control of the solids inventory as higher solids levels tended to be washed out by heavy rains. The extra treatment capacity was obtained with a relatively small cost expenditure for the chemical feed equipment and a low $170 per day increment of operating cost for alum and polymer. The success of the temporary process control technique has led us to consider it for a permanent further expansion of this plant.

Force Main System

Most of our service area is extremely flat with elevations ranging from only five to fifteen feet above sea level. The majority of the wastewater flows are pumped long distances from outlying neighborhoods to our plants through force mains. The distances pumped through the force mains approach twenty miles and the detention time in the force mains approach twenty-four hours. Such a collection system as this presents two difficult process control problems in the treatment plants—a highly septic plant influent sewage and a very marked diurnal flow pattern.

Sewage arrives at two of our activated sludge plants in a very septic condition. The dissolved oxygen of the domestic sewage is zero, its hydrogen sulfide content approximately 10 to 12 mg/l, and the color is dark black. This septic sewage causes several problems with the biological processes. First, a severe odor problem is created within the plant and extending to adjacent neighborhoods and industrialized areas. This rotten egg odor is highly objectionable to the people working and living in the area. Various methods have been tested to eliminate or reduce the odor levels. One of the early attempts was to return activated sludge to the plant headworks to freshen the raw influent sewage. Chlorination of the raw influent flow was tested both at low and at massive dosage levels. Chlorination at low dosages of 20 to 30 mg/l just prior to the headworks was completely ineffective. Massive chlorination of the septic sewage was tested at our 24 MGD contact stabilization plant having no primary clarification. Chlorine dosages of 50 to 60 mg/l applied approximately thirty minutes upstream of the plant proved to be effective in reducing the hydrogen sulfide and odor levels at the plant's headworks. However, the heavy chlorination tended to "sterilize" the influent wastewater, and chlorine residuals of 1 to 2 mg/l were carried though the plant's preliminary treatment works and into the aeration system. This chlorine residual carried into the aeration tanks knocked out the contact stabilization activated sludge process and completely prevented an active biomass from reforming during the entire six month project. Although successful from an odor control standpoint, the project had to be discontinued. We have also tested air stripping, masking agents, nitrous oxide and hydrogen peroxide as odor control measures. Of these, only hydrogen peroxide has proven successful in reducing odor levels. Hydrogen peroxide is applied at dosages of 15 to 20 mg/l at a point approximately fifteen minutes upstream of the plant's headworks. The peroxide oxidizes the sewage organics and the sewage has a bleached color when it reaches the plant. Although the hydrogen peroxide is effective, its daily operating cost of $700 per day is too expensive and we are presently pursuing other methods. A side benefit claimed for the hydrogen peroxide treatment is that influent BOD levels are reduced by about 5%.

Sludge Handling

From the standpoint of our own experience, we would say that the single most critical factor in process control of biological treatment systems is sludge handling. It is a futile and disheartening experience to attempt process control over a biological process when its related sludge handling facilities are either inoperative, inadequate or incompatable. It is impossible to maintain process control over biological systems where waste sludge cannot be effectively removed when and in the quantities required. We have found ourselves in severe problems over the past few years when the construction of our sludge handling facilities was delayed up to several years behind the upgrading and expansion of our sewage treatment plants. Under these situations, we have had to utilize innovative techniques to stretch our existing sludge handling capabilities. Although sludge handling may not generally be thought of as a biological process control measure, the overall operation of a sludge handling system is indispensible to process control of other biological treatment systems and therefore merits mention here.

Most of our older plants utilize anaerobic digestion for sludge disposal. In almost every instance, the original digestion facilities consisted of primary and secondary low rate digestion. These systems became too overloaded to function properly when the plant flows and sludge production increased. With imminent failure of the anaerobic digestors threatening to upset the biological processes, the secondary digestors were converted to primary digestors, and the sludge feed was increased to operate all digestors at higher rates. Digestor supernatant, which was formerly separated in the secondary digestors and returned to the plant flow, was either piped or trucked to sludge holding lagoons. This modification greatly increased the sludge digestion capacity of the plants and allowed their continued successful operation. Due to land limitations at one plant preventing construction of sludge lagoons, a solid bowl scroll centrifuge was installed to dewater the combined primary digestor transfer sludge. The cake was then landfilled in a much smaller area than would have been required for the liquid sludge.

Another activated sludge plant went on line four years prior to the completion of its centrifugal dewatering/incineration sludge handling facilities. In the interim, sludge handling was accomplished by converting two spare aeration tanks into aerobic digestors providing twenty days detention. The unthickened aerobically digested sludge was then pumped three miles and applied to unused open farm land. The digested sludge was spray irrigated for the first two years onto a planted grass cover crop. During a later project, the digested sludge was pumped through a 600 foot flexible hose dragged by a tractor and directly injected beneath the soil surface. The soil could be walked over immediately after injection and there was no surface runoff from this system. The system's major advantages were its lack of nuisance conditions and its soil enrichment potential.

Pilot Studies

Our organization has conducted extensive large scale pilot work over the past few years for purposes of either prototype design, interim plant upgrading, or process control. We have tested a varied assortment of proposed processes; we have either considerably altered or altogether abandoned many of the projects.

A four month pilot study was undertaken of a proposed lime clarification-biological nitrification advanced wastewater treatment process. This 100 gallon per minute pilot unit utilized a high purity oxygen activated sludge system. As a result of the study, we concluded that the proposed process would work and could produce the desired effluent, but that the biological nitrification system was too sensitive to pH and shock loading caused by upsets in the lime clarification system, and therefore the proposed system was not practical from a process control standpoint.

Over a year's pilot work was performed on all types of centrifugal dewatering devices for all types of sludges—primary, waste activated, digested, alum and lime sludges. The information gathered here was used for the design of six large centrifugal dewatering facilities. A Porteous Heat Treatment Process was piloted for three months to test its dewatering capabilities on a high strength industrial waste activated sludge. We concluded from the study that resolubilization of the sludge would create too high a return loading on the activated sludge process and would further complicate an already difficult biological process control problem. A Purifax Sludge Treatment Process was piloted at several of our plants, and one unit was installed for handling excess undigested sludge. Also tested was a flash dryer in which undigested sludge was quickly accelerated to high speeds and completely dried within a few seconds. The end product would be pelletized and used as fertilizer.

Personnel Development

One last item directly related to process control of treatment operations is personnel qualifications. It is most important to staff the wastewater treatment plants with personnel who understand and are fully qualified to control the treatment processes. We are operating sophisticated treatment plants which are designed and operated based on complex biochemical engineering principles, and it is unreasonable to expect untrained personnel to grasp the complexities of these processes and successfully operate the plants. Our organization is strongly emphasizing the need and the requirement for operators to have secondary school and advanced education. We promote and sponsor operator's attendance at training schools for wastewater treatment plant operation, and we have conducted our own school for wastewater operators for several years in addition to the on-the-job training given each operator. Also, it is just as necessary to maintain a competent staff of trained engineeres, biologists and chemists to provide the supervision and assistance required in the operation of these complex treatment facilities.

Development and Improvement of the Municipal Sewage Biological Treatment Facilities.

Yershov A., Kyghel M., Zemlyak M.,
candidates of sciences

The paper describes aeration tank types of new designs used for municipal sewage biochemical treatment, developed by the Scientific Research Institute for Municipal Economy. The paper provides technological basis of this equipment designing.

A conclusion of the necessity for choosing a certain aeration tank depending on conditions and special features of the sewage system is given.

The achievements of chemical engineering are the ground for modification of equipment and technology in the field of biochemical sewage treatment, particularly, the activated - sludge process.

There are three types of aeration tanks used in biological oxidation of contaminations by activated-sludge process: plug-flow, mixing tanks and combined systems.

Of all these types the mixing tanks are every more wide spread on a large scale that have been used lately only for high concentrated wastewater treatment. More profound research of kinetics and the pattern of sewage activated sludge biological oxidation allowed to modify this process, in particular, the methods of rapid removal of low concentrated wastewater, prevailing in suspended and colloidal form. The rapid removal process is due to the phenomena the kinetics of which is similar to adsorption process kinetics that is why such modification is called on condition as "biosorption". In municipal sewage treatment the rapid removal process in some cases is characterized by zero order equations that is over the range of low concentrated contaminations the process rate does not depend upon concentration; sewage retention time in the aeration tanks generally is determined by reactors type, that is by the hydrodynamic conditions in the aeration tank.

Thus, municipal sewage with low concentrated impurities (BOD up to 200 g/m^3) can be treated in a complete mixing system because under these conditions the activated sludge biosorption capacity is used. Municipal sewage with an average concentrated impurities (BOD from 250 to 350 g/m^3) can be treated in the plug flow reactors because complete oxidation organic matters process with active mass growth must take place. However, taking into consideration that municipal sewage impurities are mainly in the form of small dispersed suspended solids colloid matters, complete mixing aeration tanks or combined tanks can be used, under economical grounds and rational installation design. High concentrated municipal sewage (BOD from 400 to 600-800 g/m^3) can be treated in the multistage plants as activated sludge is adapted properly to changed load at every step depending on concentration changes of organic matters during the process. On the other hand the step sludge process gives the possibility to decrease sludge growth and to increase general rate and degree of process proceeding. Due to these factors, step-sludge process can be used for treatment of a low concentrated municipal sewage. On account of these conditions the various models of aeration tanks were designed: mixing systems equipped with mechanical aerators and different modifications of aeration tanks-clarifiers with activated sludge fluidized bed; multistage basins with successive compartments or fluidized beds are used as plug-flow reactors.

For treating the low concentrated municipal sewage the main part of which consists of unevenly flowing biodegrable industrial wastes contact stabilization aeration tanks equipped with turbine aerators were developed. (fig. 1).

For average concentrated municipal sewage treatment aeration tanks-clarifiers and settling tanks with sedimentation zone equipped with pneumatic and mechanical aerators begin to be used together with conventional long-form plug flow aeration tanks. These facilities provide the impurities removal (oxydation) and separation of sludge mixed liquor in one and the same technological unit. The main advantage of combined facilities is simultaneous usage of the whole activated sludge mass in sewage purification process. In view of sludge mixture increased recirculation between aeration and clarification zones there it is set practically uniform oxygenation regime and uniform activated sludge load. The above mentioned factors provide oxygenation process practically through the whole volume.

As a variety of combined aeration tanks with settling zone aeroacclerators used for a low and average concentrated municipal sewage treatment with the capacity over the range from 5000 to 50000 m^3/d can be applied.

Aeration tanks - clarifiers are rectangular basins divided baffle plate into aeration and clarification zones (fig. 2). Raw wastewater is distributed into aeration zone where it is mixed with activated sludge, and mixed liquor flows through the openings into the degazation zones and then to the clarification zones.

Aeration tanks-clarifiers include contrary to aeration settling tanks the system of baffle plates providing directed circulation of mixed liquor as a result of which downtake flow rate increases in clarification zones and activated sludge fluid-fluidized bed is formed. The presence of stable fluidized bed is due to the increased recirculation of mixed liquor on one hand, and on the other hand it promotes increased recirculation that is intensification of mass exchange between aeration and clarification zones.

In practice under the rational structural design these factors permit to transfer the impurities oxydation process to activated sludge fluidized bed that is to use it as a reactor. Increasing process removal rate in fluidized bed is explained by intensity of mass transfer under filtration mixing condition. This stage is proved by the experiments as it is shown on the fig. 3.

The curve 1 shows the process in aeration tank-clarifier with oxydation of impurities mainly in fluidized bed (ratio of fluidized bed and aeration zone volumns is 4:1); the curve 2 - depicts the process with partial transference into fluidized bed (ratio of volumes is respectively 1:0,7); the curve 3 characterizes the process in aeration settling tanks (Municipal Economy Academy types, USSR) and "Degremont" oxycontact, French firm (the data are approximated).

Hydraulic loading on activated sludge fluidized bed depended on MLSS concentration is the main factor limiting aeration tanks-clarifiers capacity. This relation is shown on the fig. 4. Optimum sludge concentration is determined in its turn, by sewage impurities concentration that is by organic matters load on the facilities. For municipal sewage the range of activated sludge concentration in aeration tanks-clarifiers is within the limits of 2 - 5 g/l that corresponds to a hydraulic loading in values 1 - 2,5 m^3/m^2 • h(0,3 - 0,7 mm/s).

Two typesizes aeration tanks-clarifiers are design for municipal sewage treatment stations of the capacity 17000 - 160000 m^3/d. Besides, aeration tanks-clarifiers designing principle is a base of long-form aeration tanks intensification by means of their reconstruction into aeration tank-clarifiers. Although aeration zone volume is too high, there is necessity to use secondary settling tanks and total biological treatment complex capacity increases. There is also some possibility of increasing activated sludge operational concentration. The calculations for reconstruction of present long-form aeration tanks into aeration tanks-clarifiers at the municipal sewage station, the Ukraine, have given the following results: according to II-32-74 total sewage retention time in aeration tanks and secondary settling tanks accounts for 13 h. at the oxydation rate in aeration tanks equal to 22,6 mg BOD$_5$/g. of sludge after the reconstruction sewage retention time in aeration tanks-clarifiers has become 7,73 h at oxydation rate 25,2 mg BOD$_5$/g of sludge/h. The secondary settling tanks can now be used for intensification of the other aeration tanks.

The hydraulic principle of aeration tanks-clarifiers desining was used to developed various technological modifications of small and average plants equipped with mechanical aerators in order to form fluidized bed.

Two compartment aeration settling tanks use step-sludge sewage treatment process at a low oxydation rate securing sludge stabilization (total oxydation process).

Aeration zone is divided into successively operating compartments. The first compartment (stage) accepts high loads levelling their changes, securing the concentration of a considerable part of impurities on the activated sludge flocs. A certain part of MLSS from the first stage compartment with the flow that is equal to the sewage flow outlets into the second stage where organic matters and the sludge grown in the first stage are mineralized by the sludge adapted to a low oxydation rate. Clarification zone and the second stage compartment have common inner recirculating flow creating activated sludge fluidized bed in this zone as in aeration tanks-clarifiers.

The first stage of two compartment aeration settling tanks is equipped with cylindrical or impeller rotor aerators; the second stage is equipped with longitudinal rotation axis cylindrical rotor aerators.

Hydrodynamic scheme of the combined aeration unit with cylindrical rotor aerator is characterized by flow lines on one plane and thus simplifying its calculation and maintenance.

The further development and modification of aeration tank-clarifiers tends to the facilities design with spread activated sludge fluidized bed surface without volume increasing and with intensified vortical circulation within the beds. This provides high hydraulic capacity of the aeration tanks-clarifiers, decreases sewage retention time and increases sewage treatment quality.

Together with combined aeration facilities CMAS-aeration tanks with secondary settling tanks are widely used; they are stable to load changes during the day. These facilities are used at small communities, towns and municipal sewage treatment plants designed for the capacity up to 7000 m^3/d with food industry wastes of high concentrated impurities, flowing from the enterprises located there. Radial type aeration basins APT and circulation oxydation ditches UOK. were developed for these purposes. Both facilities are equipped with mechanical longitudinal rotation axis rotor aerators.

APT is a cylindrical basin (fig. 5) with concentrically installed secondary settling tank. The ring space is used as an aeration compartment equipped with rotor aerators.

UOK is a circular ditch (aeration tank) with rotor aerators; secondary settling tank is situated apart from the ditch (fig. 6). The secondary settling tank is of a vertical type (fig. 7). It has intensified hydrodynamic scheme permitting to increase considerably its capacity in comparison with "orthodox" type.

The calculations of the process rates and other kinetic parameters for described new aeration facilities are based on the unified method of the USSR BUILDING STANDARDS and regulations II-32-74, however, the calculations have some peculiarities in any single case due to facilities hydrodynamic characteristics.

Practical application of the facilities is secured with a set of experimental and standard designs and unified aeration equipment.

Legend to figure 1

Contact stabilization aeration tank.
1 - sewage inlet
2 - turbine aerators
3 - return sludge inlet from secondary settling tanks
4 - discharge lines
5 - outlet of mixed liquor to secondary settling tanks
6 - contact basin
7 - stabilization basin

Legend to Figure 2

Aeration tank - clarifier
1 - clarification zone
2 - gates
3 - aeration zone
4 - overflow trough
5 - degazation zone
6 - cap
7 - trough for treated water collecting and discharging
8 - surplus sludge outlet
9 - opening
10 - aerators
11 - sewage inlet
12 - "tooth"
13 - baffle plate

Legend to figure 3

Isotherms of impurities removal in combined aeration facilities (Explanations are given in the text).

Legend to Figure 4

Activated sludge fluidized bed calculated hydraulic load dependancy on its MLSS concentration.

Legend to Figure 5

Radial type aeration basin.
1 - aeration compartment
2 - secondary settling tank
3 - rotor aerators
4 - treated water outlet
5 - MLSS outlet to recirculating pump
6 - surplus sludge outlet
7 - return sludge inlet by means of recirculating pump

Legend to figure 6

Circulating oxydation ditch
1 - shelter
2 - UOK
3 - recirculating sludge pump
4 - secondary settling tank
5 - rotor aeration tanks

Legend to figure 7

UOK secondary vertical settling tank
1 - sewage inlet
2 - distributing compartment
3 - floatting matters outlet
4 - collecting funnel
5 - toothed weir
6 - baffle plate
7 - distributing trough
8 - trough for treated water collecting and draining
9 - discharge pipe
10 - cylindrical baffle
11 - sludge outlet

Protocol

of the third Meeting of the USA and USSR delegations on the problem of Prevention of Water Pollution from Industrial and Municipal Sources (Moscow, USSR, August 22 - September 5, 1976)

In accordance with the Memorandum of the third Meeting of Joint USA-USSR Commission on Cooperation in the field of Environmental Protection (Washington, October 1975) the USA and the USSR delegations Meeting on the problems of Waste Water Treatment was held in Moscow, August 22 - September 5, 1976.

The Soviet delegation was headed by Prof. S.V. Yakovlev, Director of the Scientific Research Institute VODGEO, Honoured Scientist of the RSFSR.

The American delegation was led by Mr. J.T. Rhett, Deputy Assistant Administrator, Water Program Operations, EPA.

The list of participants is attached in Appendix I.

In the course of the Meeting the following was accomplished:

1. The Symposium "Intensification of Bio-Chemical Treatment of Waste Waters".
2. The accomplishments of the 1976 Program of cooperation were discussed.
3. Coordination of the Working program for 1977 was agreed upon.

1

At the Symposium 15 reports were delivered: 8 reports were delivered from the Soviet Side and 7 reports from the American Side.

The list of reports delivered is attached as Appendix II.

Of particular interest were reports delivered by the Soviet specialists on technical oxygen usage for industrial waste water treatment and bio-chemical treatment of highly concentrated waste waters as well as the reports delivered by American specialists on combined physical-chemical and bio-chemical treatment processes and on designing of bio-chemical treatment systems with the use of oxygen.

The delegations have agreed that each side will publish all reports in the necessary number of copies in its own language prior to February 1, 1977 and will distribute them among interested organizations. The sides will exchange 10 copies each of the published Proceedings of the Symposium.

2

In the course of the Meeting the specialists discussed the results of current researches carried out in accordance with the Program of cooperation and exchanged scientific and technical literature.

3

The delegations determined and coordinated the program of cooperation for 1977 (Appendix III).

The sides have agreed that the Symposium "Physical-Mechanical Waste Water Treatment Facilities" will be held in the USA, April 3-17, 1977.

The following has been agreed about the preparation of the forthcoming Symposium:

—each side will present 5-7 reports at the Symposium;

—the sides will exchange the report titles by February 1, 1977.

—the texts of the reports will be exchanged in Russian and in English prior to March 1, 1977.

Organizational Work for carrying out the Symposium "Recycling Water Supply Systems and Reuse of Treated Effluents at Industrial Enterprises" to be held in the USSR, September 18 - October 2, 1977 will be considered in the course of the delegation meeting in April 1977.

In 1977 an exchange of specialists will be carried out:

—of Soviet specialists in the USA on the problems of waste water treatment, and

—of American specialists in the USSR on the problem of waste water treatment and reuse.

The detailed exchange program will be agreed five months prior to the date of the participants' departure. This exchange will be carried out on the basis of equal and "receiving-side-pays" basis.

In the course of this visit to the USSR the American delegation visited industrial and municipal wastewater treatment plants in Ufa, Leningrad, Shekino, Baikalsk and Tashkent, and a number of scientific research and project institutes in Moscow, Leningrad and Tashkent.

Both sides expressed their satisfaction that the Meeting was conducted in an atmosphere of friendship and mutual understanding thus contributing to the further development and strengthening of cooperation in the field of environmental protection.

This protocol was signed on September 4, 1976 in two copies, in Russian and English, both texts being equally authentic.

From the Soviet Side	From the American Side
S.V. Yakovlev *Chief of Delegation*	**John T. Rhett** *Chief of Delegation*

Appendix I

List of Participants from the Soviet Side

S. Yakovlev
Director, VNII VODGEO, Prof. Chairman of the USSR Delegation

D. Slavolyubov
Chief of the Department, Glavpromstroyproekt.
GOSSTROY USSR

I. Skirdov
Head of the laboratory, VNII VODGEO cand. techn. sci.

V. Ponomarev
Head of the laboratory, VNII VODGEO cand. techn. sci.

P. Kandsas
Head of the laboratory, VNII VODGEO cand. techn. sci.

I. Myasnikov
Head of the Sector, VNII VODGEO cand. techn. sci.

V. Shvetzov
Head of the Sector, VNII VODGEO cand. techn. sci.

A. Nechaev
Senior Researcher, VNII VODGEO cand. techn. sci.

M. Voronina
Senior Engineer, VNII VODGEO

N. Nelubina
Interpreter
GOSSTROY USSR

List of Participants from the American Side

J. Rhett
Chairman of the US Delegation Deputy Assistant Administrator for Water Program Operations, EPA.

A. Paretti
Consultant, Water Program Operations.

A. Cywin
Senior Science Advisor, Office of Water & Hazardous Materials.

W. Lacy
Senior Engineering Advisor, Office of Research & Development.
W. Rosenkranz
Director, Waste Management Div.
F. Sebastian
President, Waste Water Equipment Manufactures Association.
F. Harper
General Superintendent, Orange County Sanitation District.
W. Love
General Superintendent
Hampton Roads Sanitation District.
B. Sumner
President, U.S. Council of Consulting Engineers.
A. Malyshev
Interpreter, Colorado College.

Appendix II

Reports

of reports presented at the USSR-USA Symposium "Intensification of Bio-Chemical Treatment of Waste Waters"

From the Soviet Side

1. Yakovlev S.V., Skirdov I.V., Shvetzov V.N., Rogovskaya C.I. (VNII VODGEO) "Kinetics of Biochemical Oxidation".
2. Skirdov I.V., Shvetzov V.N., Bondarev A.A., Lurie B.I., Bereyskina I.G., Katkova S.E. (VNII VODGEO, Complex "ASOT" in Shekino) "Operation Experience of Oxytanks".
3. Shvetzov V.N., Morosova K.M., Gubina L.A. (VNII VODGEO) "Biochemical Treatment of Wastewaters from W001-Scouring Operations".
4. Yakovlev S.V., Karjuhina T.A. (MISI) "Biological Waste Water Treatment in the Presence of Steroid Compounds".
5. Shifrin S.M., Mishookov B.G., Ivanov G.V., Goloobovskaya E.K. (LISI) "The Trends in Intensification in Biochemical Treatment of High Density Wastewater".
6. Gerber V.Y. (Bash. NII NP) "Facilities Improvement for Biochemical Treatment of Petroleum Refinery Wastewaters".
7. Skirckyavichus R.L. (The Ministry of Municipal Economy of the Lithuanian SSR) "Studies of Artificial Aeration in the Lithuanian SSR".
8. Yershov A., Kyghel M., Zemlyak M. (NIKTI GH) "Development and Improvement of the Municipal Sewage Biological Treatment Facilities".

From the American Side

1. A. Cywin (EPA) Enchancement of Biological Waste Water Treatment by Chemical Addition in the Petro-Chemical Industry.
2. W. Lacy (EPA) "Steel Industry Waste Water Treatment Using Biological-Chemical Technology".
3. W. Rosenkranz (EPA) "Biological Methods for Control of Nitrogen in Municipal Waste Waters".
4. F. Sebastian (EPA) "Improvements for Pulp and Paper and Municipal Treatment Processes".
5. F. Harper (EPA) "A Comparison of Conventional Activated Sludge Process and Pure Oxygen Activated Sludge Process for a 75 MGD Secondary Treatment Facility".
6. B. Sumner (EPA) "Report on the State of the Art of Biological Waste Treatment in the Organic Chemical Industry in the United States".
7. W. Love (EPA) "Analytical and Process Improvements in Municipal Bio-Chemical Wastewater Treatment".

Appendix III

Program

USA-USSR Cooperation of Working Group on Prevention of Water Pollution from Industrial and Municipal Sources

No.	Title	Form of Work	Responsible for from the USSR	Responsible for from the USA	Time	Expected Results
I.	Modernization of existing and development of new combined facilities with high efficiency for wastewater treatment, including hydrocyclones, multistage settlers, flotators, facilities with utilization of technical oxygen, investigation of usage of flocculants and coagulants.	Joint development of themes, scientific information and specialists delegation exchange.	VNII VODGEO Gosstroy USSR	EPA	1978	Improvement of the efficiency of existing and development o new treatment facilities, reduction of space for location, reduction of reagents and cost price of waste water treatment
	Development of hydrocyclones and flotation facilities; schemes of usage of coagulants.	Symposium on "Physical-Mechanical Waste Water Treatment Facilities" (USA, Cincinnati, April 3-17, 15 days, 8 specialists)	VNII VODGEO			

No.	Title	Form of Work	Responsible for from the USSR	 from the USA	Time	Expected Results
	Development of tubular and plate settlers and facilities with utilization of technical oxygen; schemes of usage of flocculants.	Symposium on theme: "Recycling water supply systems and reuse of treated effluent at industrial enterprises" (USSR, Moscow, September 18-October 2, 1977, 15 days, 8 specialists).		EPA and appropriate industries		
2.	Intensification of wastewater treatment process in petrochemical, chemical, petroleum refining, pulp and paper industries, and metallurgical industry.	Information and delegation exchange	VNII VODGEO Gosstroy USSR	EPA	1978	Increasing of wastewater treatment efficiency of existing treatment plants, introduction of new treatment schemes, maximum usage of treated effluents in recirculation.
	Intensification of wastewater treatment process in petroleum refining industries, and metallurgical industry.		VNII VODGEO			
	Intensification of wastewater treatment process in petrochemical and pulp and paper industries.			EPA and appropriate industries		
3.	Development of highly efficient methods and facilities for removal of nutrients and treatment of municipal wastewaters; usage of treated effluents in recycling systems at industrial enterprises.	Joint development of themes, information and delegation exchange	VNII VODGEO Gosstroy USSR	EPA	1977	Development of new treatment facilities for prevention of water basin eutrofication and development of new treatment systems with maximum usage of treated effluents in recycling systems at industrial enterprises.
	Development of methods and facilities for removal of nutrients and treatment of municipal wastewaters.		VNII VODGEO			
	Usage of treated effluent in recycling systems at industrial enterprises.			EPA and appropriate industries		
4.	Treatment of wastewater sludges.	Information and delegation exchange	VNII VODGEO Gosstroy USSR	EPA	1977	Reduction of cost price of waste water sludge treatment, increasing of treatment facilities efficiency.
	Stabilization and dewatering of wastewater sludges.		VNII VODGEO			
	Technology and facilities for utilization and treatment of wastewater sludges.			EPA and appropriate industries		
5.	Exchange of two Soviet specialists for 2 months in US on the problem of usage of technical oxygen at biological waste water treatment plants.	Study of research work of American companies and organizations, participation in scientific studies.	VNII VODGEO Gosstroy USSR		III Quarter 1977	Studying of the USA experience in the field of waste water treatment.
	Exchange of two American specialists for 2 months in the USSR on the problems of wastewater treatment and reuse.	Acquaintance with research work of the Soviet organizations and institutes, participation in scientific studies.		EPA	III Quarter 1977	Studying of the USSR experience in the field of waste water treatment.

NOTE: Companies to be involved in carrying out the joint activities on the American Side will be named at the 4-th meeting of specialists, April 1977, in the USA.

Appendix IV

Itinerary

for the US-Delegation Stay in the USSR at the US-USSR Symposium" Intensification of Bio-Chemical Treatment of Waste Waters".

Sunday, August 22

Flight CY-242 19:10	Arrival at the airport. Putting up at the hotel.

Monday, August 23

9:00	Discussion on the program for the US-Delegation stay in the USSR.
9:15	Opening ceremonies of the symposium
9:45	Yakovlev S.V., Skirdov I.V., Shvetzov V.N., Rogovskaya C.I. (VNII VODGEO), "Kinetics of Biochemical Oxidation."
10:25	Cywin A. (EPA) "Enhancement of Biological Waste Water Treatment by Chemical Addition in the Petro-Chemical Industry."
11:05	Discussion.
11:20-11:35	Break.
11:35	Shifrin S.M., Mishookov B.G., Ivanov G.V., Goloobovskaya E.K. (LICI)" The Trends in Intensification in Biochemical Treatment of High Density Wastewater."
12:15	Lacy W.J. (EPA) "Steel Industry Waste Water Treatment Using Biological-Chemical Technology."
12:55	Discussion.
13:10	Break.
14:10	Gerber V.Y. (Bash. NII NP) "Facilities Improvement for Biochemical Treatment of Petroleum Refinery Wastewaters".
14:50	Rosenkranz S. (EPA)" Biological Methods for Control of Nitrogen in Municipal Waste Waters."
15:30	Discussion.
15:45	Skirdov I.V., Shvetzov V.N., Bondarev A.A., Lurie B.I., Bereyskina I.G., Katckova S.E. (VNII VODGEO, SHekinsky Complex "ASOT") "Operation Experience of Oxytanks".
16:25	Discussion.

Tuesday, August 24

9:00	Sebastian F.P. (EPA) "Improvements for Pulp and Paper and Municipal Treatment Processes".
9:40	Yakovlev S.V., Karjukhina T.A. (MISI) "Biological Waste Water Treatment in the Presence of Steroid Compounds.)
10:20	Discussion.
10:35	Break.
10:50	Harper F. (EPA) "A Comparison of Conventional Activated Sludge Process and Pure Oxygen Activated Sludge Process for a 75 MGD Secondary Treatment Facility".
11:30	Skirckyavichus A.L. (The Ministry of Municipal Economy of the Lithuanian SSR, KPI) "Studies of Artificial Aeration in the Lithuanian SSR;"
12:10	Discussion.
12:25-13:25	Break.
13:25	Sumner B. (EPA) "Report on the State of the Art Biological Waste Treatment in the Organic Chemical Industry in the United States
14:05	Shvetzov V.N., Morosova K.M., Gubina L.A. (VNII VODGEO) "Biochemical Treatment of Wastewaters from Wool-Scouring Operations".
14:45	Discussion.
15:00	Love B(EPA) "Analytical and Process Improvements in Municipal Bio-Chemical Wastewater Treatment."
15:40	Discussion.
16:00	Adjournment.

Wednesday, August 25

10:00	Visit to the Scientific Research Institute of Municipal Water Supply and Wastewater Treatment.
Flight N 341 14:55	Leaving for Upha.
18:40 (16:40 Moscow time)	Arrival in Upha. Putting up at a hotel. Rest.

Thursday, August 26

10:00 Acquaintance with Treatment Facilities of Petroleum Refinery Plant in Upha.

Flight 340 20:05 Leaving for Moscow.

20:00 Arrival in Moscow.

23:55 Leaving for Leningrad by train.

Friday, August 27

8:25 Arrival in Leningrad, putting up at a hotel.

11:00 Visit to the Leningrad Department of the Institute "Sojusvodocanalproject".

15:00 Acquaintance with Experimental Pulp and Paper Complex in Krasnogorsk, VNPO BYMPROM.

Saturday, August 28

Sightseeing excursions around Leningrad.

Sunday, August 29

Sightseeing excursions around Leningrad.

23:55 Departure for Moscow by train "Red Arrow"

Monday, August 30

8:25 Arrival in Moscow.

12:00 Visit to Shekino, visit to treatment facilities of the Complex "ASOT".

Flight 121 19:59 Leaving for Irkutsk.

Tuesday, August 31

8:05 Arrival in Irkutsk, putting up at a hotel.

10:00 Departure for Baikalsk by buses.

14:00 Visit to the treatment facilities of Pulp and Paper Complex.

17:00 Leaving for Irkutsk by buses.

Wednesday, September 1

Flight 3719 15:35. Leaving for Tashkent.

20:05 Arrival in Tashkent, putting up at a hotel.

Thursday, September 2

10:00 Visit to the department of VNII VODGEO.

15:00 Acquaintance with the Salar Aeration Plant.

Friday, September 3

Flight 5087 8:00 Leaving for Samarkand.

8:55 Arrival in Samarkand. Sightseeing excursions around Samarkand.

Flight 688 20:24 Departure for Moscow.

22:44 Arrival in Moscow, putting up at a hotel.

Saturday, September 4

10:00 Excursion to Archangelskoye.

17:00 Signing the protocol. Final Meeting.

Sunday, September 5

Departure.

References

Ierusalimskii, N.K., 1967, Academy of Science, USSR, Series of Biology, No. 3,339.

Michaelis L., Menten M.L., 1913, Biochem 7,49,333.

Monod J. Annual Review of Microbiology, 1949, 3,371.

Hinshelwood, C.N., The Chemical Activities of Bacteral Cee. Clarendon Press. Oxford, 1946.

Harbert D., 1961, Sonety of Chemical Ind. Monogr., N 12,25-5.

Dawning, A.Z., Wheatliand A.B., Paper Press to Mid. Pranch. of Inst. of Chem. Eng. 1960.

Benedek, P., 1967, VITUKI Report, N 20, Budapest.

Gyunter, L.I., Zaprudskiy, V.S., 1971, Collection Microbiological Industry, No. 5.

Garrett, T.M., Sawejer, C.N., 1961, Ind. Waste Contr. Fed. N 33, 800-816.

Eckenfelder, W.W., 1966, Ind. Water Poll. Contr. New-York, Toronto, London.

McGabe, B.I., Eckenfelder, W.W., 1961, J. Wat. Poll. Contr. Fed. 33,3,258.

Zhukov, A.I., Karelin Ya. A., Kolobanov, S.K., Yakovlev, S.V., Sewerage System "Stroyizdat," Moscow, 1969.

Wuhrman, K., e.a. 1959, Schweiz, Ztschr. Hydrol., 20,284.

Yeilevich, M.A., Korovin, L.N., Shvytov, I.A., Inf. Biol II, All Union School on Mathematical Modeling in Biology. USSR Academy of Science, Pushchino, 1975.

Repin, V.N., Materials of the Scientific-Methodological Conference of Aspirante MISI. Collection of Works, No. 62, Third Edition, Moscow, 1969.

Karelin, Ya. A., Zhukov, D.D., Rozanov, V.L., Research on Waste-Water Treatment, Collection of Works, MISI, No. 66, Moscow, 1970.

Smith, D.B., Sex. and Ind. Wastes, 24, 9 Sept., 1952.

Okun, D.A., Lynn, W.R., Biol. Treatment of Sw. and Ind. Wastes. I. Aerobic Oxidation. R.P.C. New-York, 1956.

Bennet, G.F., Kempe, L.L., Chem. Geng. Poc. Symposium Series, 1967, 63, N 78.

Joung, H.L., J. Bacterial, 1969, 97, N 3.

Goftlieb, S.F., J. Bacterial, 1969, 92, N 4.

Okun, D.A., Sewage Works Journal, 21, 1949.

McKinney, R.E., Pfeffer, S.T., Water and Sewage Works, October, 1965.

Kariuskiy, A.A., Laskov, Yu.M., 1958, News of Higher Institutes of Learning Construction and Architecture, 10.

Gilsderman, Yu.I., 1969, Mathematization of Biology, Moscow, "Znaniya"

Iyervsalimskiy, N.D., Neronova, N.M., 1965, DAN USSR 161, No. 6, 1437.

Vestali, D. 1972, Ferentative Catalyst, Moscow, "MIR"

Muzchenko, L.A., Gubin, V.A. Kautere, V.M., 1973, Collection of Mathematical Modeling of Microbiological Processes, Pushchino on the Oka.

Table I

Operation data of counter-flow aeration tanks with air and oxygen supply and acetone as a substrate

Lest Number	MLVSS g/l	D.O. Concentration mg/l	Wastewater COD Influent	mg O^2/l Effluent	Organic Matter COD m^3/day	Specific Oxidation Rate mg COD g/hour
Oxygen Supply						
1	2.81	11	3962	132	7544	111.6
2	3.01	7.3	4906	154	9333	129.1
3	3.27	17	4610	174	8692	110.2
4	3.83	10	4264	99	8223	87.0
5	3.41	10	4850	61	9417	114
6	2.46	14	3468	71	6727	114
7	3.31	7.3	4667	174	11023	141.6
8	4.10	14	5781	102	9034	91.6
9	2.9	14	4089	125	7795	111.6
10	3.29	16.5	4638	166	8819	111.6
11	2.5	13	3525	94	6768	112.5
12	3.6	13.8	5076	981	9307	107.9
	mean:	12.7			8538	111.9
Air Supply						
1	2.6	2.5	1070	69	2402	38.5
2	2.95	2.5	1280	54	2452	31.6
3	3.0	2.4	1026	84	3982	42.5
4	3.1	2.3	1345	76	2538	34.1
5	3.4	3.1	1475	84	2782	34.1
6	3.47	2.7	1505	307	2486	28.0
7	3.1	3.2	1007	125	1760	23.0
8	5.73	3.3	2508	55	1920	38.4
9	5.81	3.6	2257	120	4280	30.0
10	6.57	3.2	2851	104	5502	34.8
11	2.75	3.0	1193	31	2397	34.8
12	2.92	3.0	1898	23	3731	40.3
13	3.21	3.4	2808	61	5037	65.4
14	3.05	3.2	2318	46	1502	61.2
	mean:	2.98	—	—	3400	39.4

Summary 2

Substrates	Designation on figure	Chemical formula	Molecular weight	C organic carbon mg/mg matter	Water solubility g/l	COD mg O/mg substance	BOD mg O/mg substance	Ratio BOD/COD	Difference COD-BOD	Oxidation specific rate mg BOD/g sl hour	V_{max} mg O_2/g • hour	K_s mgBOD/l	COD-BOD/COD		Sludge increase g/g	O.D. by Varburg apparatus mm/mg sl • hour	DGA (DTA) mg sl by summary	The number of bacterias for oxidation of substance into 1g of dry sludge
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Methanol	1	CH_3OH	32.04	0.37		1.56	1.02-1.2	68-80	0.36	23-54x	830	1.67	0.26	-	-	-	12.5	3.10^{14}
Ethyl alcohol	2	C_2H_5CH	46.05	0.52		1.84	1.38	75	0.46	16.6x	670	1.5	0.25	-	-	-	-	-
Propyl alcohol	3, 5	C_3H_7OH	60.09	0.59		2.3-2.4	1.62	70	0.72	14.1-21.5	200	143	0.32	0.022	0.11	11.6	12.5	3.10^{16}
Isopropyl alcohol	6	$(CH_3)CHOH$	60.09	0.59		2.22	1.54	69.0	0.8	16.7	17	16.0	0.33	0.055	0.32	7.7	16.8	3.10^{12}
Butyl alcohol	4	C_4H_9OH	74.08	0.65	90	2.40	1.60	66.0	0.8	16.6x	260	3.9	0.57	-	-	-	-	-
Propyonic aldehyde	7	CH_3CH_2CHO	58.08	0.62	200	2.20	1.20	65	1.0	11.5	73	29	0.45	0.007	0.55	8.6	9.8	4.10^{9}
Propionic acid	8	$CH_3CH_2CO_2H$	74.08	0.48		1.51	1.19	79	0.32	22.1	45	16	0.21	0.038	0.25	10.5	5.6	5.10^{9}
Propylen glycol	9	$CH_3CHOHCH_2OH$	76.09	0.48	x.p.	1.57	1.20	76.5	0.35	24.5	125	156	0.24	0.106	0.16	11.0	15.0	3.10^{14}
Benzalcohol	10	$C_6H_5CH_2OH$	108.14	0.78	40	2.51	2.04	81	0.47	35-38	158	9.6	0.19	0.040	0.31	28.6	18.4	3.10^{14}
Benzaldehyde	11	C_6H_5CHO	106.13	0.8	3.3	2.41	2.1	87.5	0.31	26	202	31.4	0.14	-	0.24	24.0	14.3	3.10^{5}
Benzoic acid	12	C_6H_5COOH	122.13	0.69	3.0	2.0	1.67	83.5	0.33	29.3	-	-	-	0.101	-	-	-	-
Pyrocatechol	12	$C_6H_4(OH)_2$	110.12	0.65	451	1.9	1.46	78.5	0.43	16.3-15.7	393.7	21.65	0.23	0.143	0.62	17	23.5	3.10^{10}
Resorcipol	13	$C_6H(OH)_2$ meta	110.12	0.65	229.0	1.89	1.5	79.3	0.39	16.0	573	12.3	0.19	0.069	1.93	21	15.8	3.10^{10}
Hydroquinone	14	$C_6H_4(OH)_2$ gapa	110.12	0.65	59	1.86	0.15	8	0.43	8-10	41.5	0.786	0.62	-	1.08	19	-	3.10^{8}
Acetone	15	$(CH_3)_2CO$	58.08	0.62		2.17	1.68	77.4	0.49	59-13.8	-	-	0.23	-	-	-	-	-
heptanol	16	$CH_3(CH_2)_5CH_2OH$	116.21	0.72	0.9	2.7	1.8	66.7	0.9	13.6	-	-	-	-	-	-	11.5	5.10^{10}
lactic acid	17	$CH_3CHOH\ CO_2H$	90.08	0.39		1.07	0.95	85.4	0.12	46	-	-	-	-	-	-	-	-
acetylfornic acid	18	$CH_3CO\ CO_2H$	88.06	0.41		0.91	0.64	70.05	0.27	49.6	-	-	-	-	-	-	-	-
ortho-cresol		$CH_3C_6H_4OH$	108.14	0.77	24.5	2.31	1.78	78	0.63	41.5	-	-	-	-	-	-	-	-
meta-cresol		$CH_3C_5H_4OH$	108.14	0.77	23.5	2.45	1.84	75	0.58	42	-	-	-	-	-	-	-	-
para-cresol		$CH_3C_5H_4OH$	108.14	0.77	1.94	2.45	1.84	75	—	—	-	-	-	-	-	-	-	-